

PUBLISHABLE SYNTHESIS REPORT

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PROJECT No : BE- 3142-89

TITEL : Development of fabrication technology for the
production of metal oxide based sensors

PROJECT
COORDINATOR : IMEC

PARTNERS : NTUA
ARMINES
CORECI
WINTER

STARTING DATE : 01/08/1 991

DURATION: 53 MONTHS

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I. EXECUTIVE SUMMARY

This report gives a general overview of the technical and scientific progress made in the project and summarizes the main conclusions.

The general aim of the DEMOST project was to provide production techniques and eventually production source(s) for reliable and fast responding sensing devices which are selective and sensitive towards specific species, The specific objectives were:

- the investigation of the potential of engineering SnO₂, In₂O₃ and ITO or sandwiches of these materials as gas sensing materials;
- the investigation for the suitability of thin and thick film produced with the mentioned materials as gas sensing films;
- the investigation of these films and related solid state structures for the detection of gases in terms of fabrication processes, process parameters and resulting gas sensitivity;
- the investigation of new reliability tests, aiming at fast detection of process and product failures;
- the demonstration of the most successful structures as gas detectors for a number of gases on lab scale;
- and finally, the demonstration of the most promising sensors with the required mechanics and electronics in a prototype apparatus by field tests in such a way that a production source for these devices could be established.

In order to realise these objectives following approach was adopted:

During the first 2 years the emphasis was on material and process development. Five production techniques for the realization of SnO₂, In₂O₃ and ITO films were studied and evaluated with respect to their process parameters and processability. The physical and chemical characterization of the surface and bulk material was carried out, in order to understand the reaction mechanism taking place at the gas-solid interface,

The specific activities of this project part are :

- Film fabrication by thick film , metallo organics, chemical vapour deposition, reactive sputtering and reactive evaporation technique.
- Film characterization : mechanical, structural, physical and chemical

During the third and fourth year of the project main emphasis was put on sensor characterization and evaluation of prototypes. Initially sensor characteristics with respect to CH₄, C₂H₅OH and CO gas mixtures as a function of moisture level and temperature would be measured. At that period of the project WINTER Gasanlage GmbH replaced the VYNCKIER company (the Greek ELLTEC company was not able to sign the consortium agreement and did not take part in the project). Due to the project participation of the WINTER company a direct link to the CENELEC Technical Committee TC 116 active in preparing an European "standard for gas detection in domestic premises was realised. The technical specifications put forward by the CENELEC Technical Committee TC 116 were , taken as a new and extra objective by the consortium.

Of all the objectives this extra objective was not met in the project, and requires an extra research effort.

Fundamental ageing studies were performed in order to elucidate the failure mechanism eventually present in the prototypes.

The activities during this second period were:

- Sensor characterization of the resistive and diode type sensors, full electrical characterization and ageing and reliability study of the sensortypes developed during the project.
- Prototype characterization which comprises the production of the prototypes, the thermal design of the sensors, the fabrication of a functional prototype including field tests.

II. OBJECTIVES OF THE PROJECT

The general aim of the DEMOST project is to provide production techniques and production source for reliable and fast responding sensing devices which are selective and sensitive towards specific gaseous species.

Therefore the specific project objectives were:

- 1) To investigate the potential of engineering of SnO₂, In₂O₃ and ITO or sandwiches of these materials as reliable and selective gas sensing materials;
- 2) To investigate the suitability of thin and thick films produced with mentioned materials as reliable and selective gas sensing films;
- 3) To investigate the films and related solid state structures for the detection of gases in terms of fabrication processes, process parameters and resulting gas sensitivity;
- 4) To investigate new reliability tests, aiming at fast detection of process and, product, failures;
- 5) To demonstrate the use of the most successful structures as gas detectors for a number of gases on lab scale;
- 6) To demonstrate the most promising sensor with the required mechanics and electronics in a prototype apparatus by field tests in such a way that a production source for these devices can be established.

III. SCIENTIFIC AND TECHNICAL APPROACH

At the time of writing the proposal following technical benefits were expected from the DEMOST programme:

- The sensitive material is made of ceramic semiconducting materials, which allow further miniaturization in a planar technology and as such uses less materials compared to the pellets used by the Japanese competition.
- The construction envisaged allows less power consumption (some 100 mW), which results in a product that will be easier to integrate with the interface electronics. As a consequence, first steps towards "smart" gas sensors are made possible.

The research was therefore performed in two phases;

Year 1 & 2: film fabrication and characterization

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The specific activities of this project part are:

- Film fabrication by thick film, metallo organics, chemical vapour deposition, reactive sputtering and reactive evaporation technique.
- Film characterization: mechanical, structural, physical and chemical

Year 3 & 4: sensor and prototype characterization

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IV. TECHNICAL RESULTS

CHAPTER 1. FILM FABRICATION AND CHARACTERIZATION

1. THICK FILM FABRICATION AND CHARACTERIZATION

In this task the following topics were studied

- synthesis of the basic tin dioxide material,
- characterisation of the powders,
- characterisation of the thick film inks,
- fabrication procedure
- methodology for material selection

1.1, Design methodology

The design and development of materials for use in gas sensors is a complex matter. The realisation of a sensor element with the desired gas sensitivity and especially the required selectivity can not be fully predicted on theoretical grounds. The variety and synergy of physico-chemical processes that influence the detection process imply that a variation in a single process parameter influences several important characteristics.

A lack of theoretical foundation limits the prediction and focussed design of semiconducting metal oxide based gas sensors. This results in the necessity for the empirical development of such elements, an approach which will be successful if based on a statistically founded design strategy

Two types of sensors have been realised in thick film technology, namely *one* based on palladium loaded tin dioxide and another based on vanadium loaded tin dioxide.

The formation of a gas sensitive film' using a screen print technology requires a number of manipulations, with a number of process parameters which can be chosen freely. Starting from a basic material, the following process sequence has been used:

drying, calcination, milling, doping, dispersing, screen printing and firing.

Since it is common use to rely on standard procedures and techniques for the last three steps, the calcination and doping parameters were considered as variable in this project. Especially the influence of the duration of calcination, of the calcination temperature and of the concentration of the dopants has been studied for the two doping systems, based on palladium and vanadium compounds respectively, Because of the large amount of possible parameter combinations the experiments were planned according to a so-called central composite design in a three dimensioned factor space.

A result of this central composite design approach is shown in figure 1

2. METALLO-ORGANIC FABRICATION AND CHARACTERIZATION

2.1 Metallo organic materials

A metallo-organic paste looks like a very viscous solution and contains no solid particles. In general the paste consists of an active material and a thickening agent. The active material is mostly a metallo-organic compound, Increasing the temperature results in a decomposition of the compound into a powder of the corresponding metal oxide, usually with a very high surface area. The thickening agent is a polymer solution of specially treated ethylcellulose free of inorganic salts. The organic solvent is an alcohol with a low vapor pressure and must be compatible with the polymer as well as with the metallo-organic material. The polymer solution acts as a temporary binder to make a screen printable paste. During the firing step the polymer disappears by pyrolysis. The major problems which appear during the paste fabrication are due to the rather high sensitivity to

hydrolysis of the active-material and the interactions of the active material with the polymer solution, resulting in non-homogeneities of the paste.

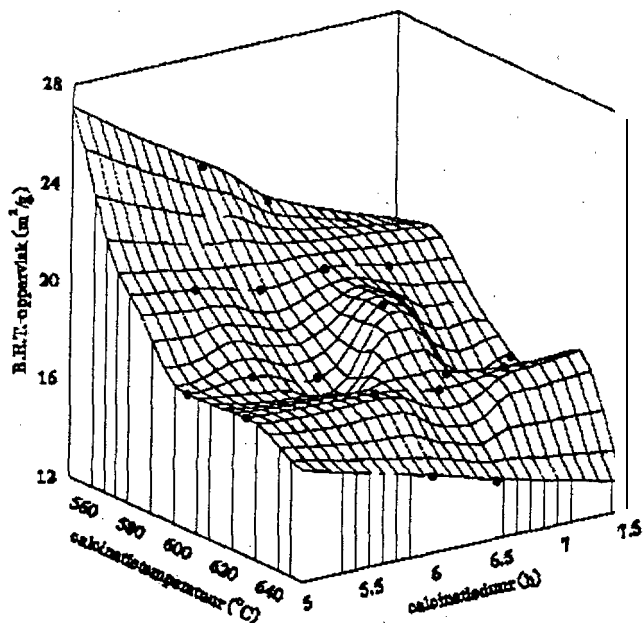


Fig. 1: B.E.T. -surface as a function of process parameters.

2.2 Metallo-organic paste preparation

The tin-metallo-organic paste is made starting from tin(II) 2-ethylhexanoate. Mixing with a polymer solution of ethylcellulose in 2-ethylhexyl alcohol results in a paste with a viscosity of approx. 30 Pas which is stable up to the 4% Sn.

In the case of iridium, the active material is iridium chloride because the metallo-organic products of iridium are not common. Iridium chloride is a white crystalline powder and not useful in this way. This problem has been overcome by the transformation of iridium chloride to a suitable soluble product by reaction with 2-ethylhexyl alcohol. The viscosity of the solution is adjusted to 30 Pas by adding ethylcellulose polymer. In this way a stable iridium-organic paste with 2% Ir has been prepared.

3. SPUTTERED FILM FABRICATION AND CHARACTERIZATION,

3.1 Film fabrication methods.

Deposition of SnO_x and InO_x films was performed with a Leybold Z-400 planar magnetron sputtering system, which was d.c. operated in a controlled, high purity Ar- O_2 mixture. Films were fabricated at a relatively high total gas pressure of approximately 1.0×10^{-2} mbar. The substrate holder was at a distance of 7 cm from the 10 cm in diameter target. The total power into the target was 115 W with a total current of 0.36 A, thus achieving a deposition rate of approximately 100 nm/min.

Deposition of SnO_x and InO_x films was carried out on Al_2O_3 (96%) and glass substrates with dimensions 12x26 mm, heated at 300 °C, a temperature which ensures that the film consists mainly of [1 10] crystallite. Argon flow was adjusted manually at 20 ml/min, while oxygen intake was controlled by a Plasma Emission Monitoring control unit, so that the intensity of the tin emission line remained constant. An O_2 flow around 30 ml/min is found to give an appropriate oxygen to tin ratio so that the films fabricated can function as sensors (low oxygen to tin ratio gives metallic films and high oxygen to tin ratio gives highly resistive films). The sputtering system was operated in constant current mode. Different film thicknesses were tested, from 10 to 4000 nm and films with a thickness of 1000 nm (10 min sputtering time) were found to exhibit satisfactory mechanical and electrical properties. This method was found adequate for the fabrication of reproducible films, exhibiting the same electrical properties within a 10% tolerance.

Films deposited on alumina (96%) substrates were found to exhibit good mechanical properties, in contrast to films deposited on glass substrates. Better film adhesion on alumina substrates is attributed to its higher "surface roughness. Films thinner than about 200 nm on alumina substrates are discontinuous.

Sputtering conditions were investigated, in order to fabricate films sensitive to gases of interest. The effect of deposition temperature (film crystallinity), argon and oxygen flow during sputtering (film stoichiometry), total pressure and film thickness on film properties were studied.

4. CVD FILM FABRICATION AND CHARACTERIZATION,

Published work concerning gas sensors has proved the great influence of the micro structure of such materials on the electrical performances. The challenge in this project was to obtain high selectivities towards some gases with the best stabilities (no long term drifts). The large use of tin dioxide as sensing materials depends certainly on two kinds of properties:

- i) its intrinsic electronic properties resulting of bulk defects (non-stoichiometry SnO_{2-x});
- ii) its textural properties which allow special micro structures (fine grains).

In previous *studies* concerning sintered materials obtained from cold pressed tin dioxide powders, it has been pointed out that there is an effect of grain size and grain boundaries on the electrical conductivity. The difficulty of such investigations is to separate the different contributions to the electrical conductivity: electrical contacts, intrinsic resistance of a grain, and grain boundaries. A solution to this problem is to elaborate the material as thin films.

One of the main interesting points is the possibility to change the morphology and the structural properties of the films by varying the deposition parameters and to correlate the influence of some deposition parameters with the electrical properties and obviously with the gas sensors performances.

From the point of view of industrial development of gas sensors, the advantages of thin films technics are clear: miniaturisation (power reducing), microelectronic compatibility (multi sensors), mass production, reproducibility . . . Nevertheless this development depends on the perfect control of the deposition process. This can be

achieved especially by the understanding of phenomena and the correlations between the deposition parameters, the micro structural properties, and the electrical performances.

S.E.M. micro graphs obtained from fractures of very thick films (several microns deposited onto silicon) show that the macroscopic structures depend on the deposition temperature (figure 2). In all cases the adherence to the substrate was good.

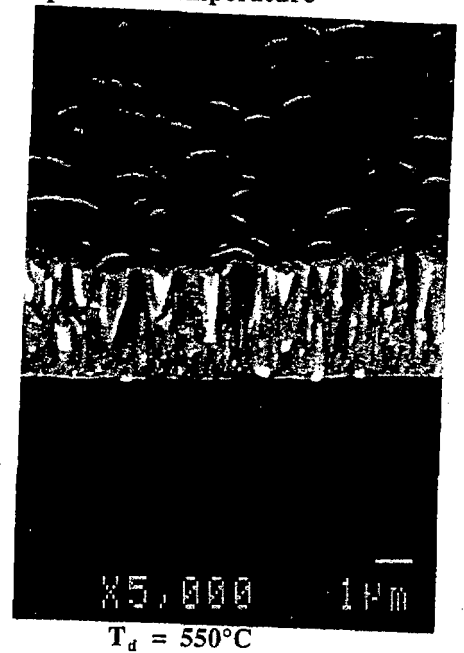
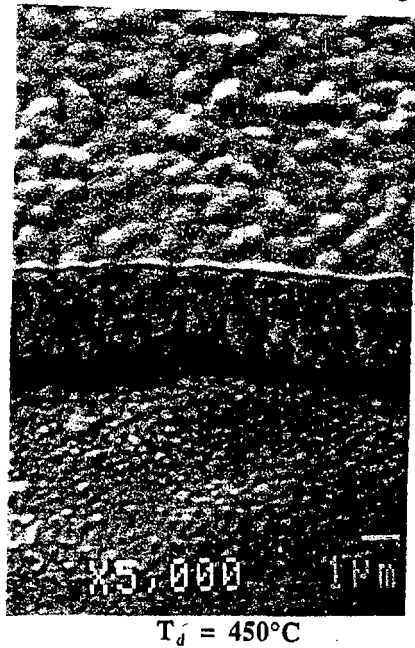
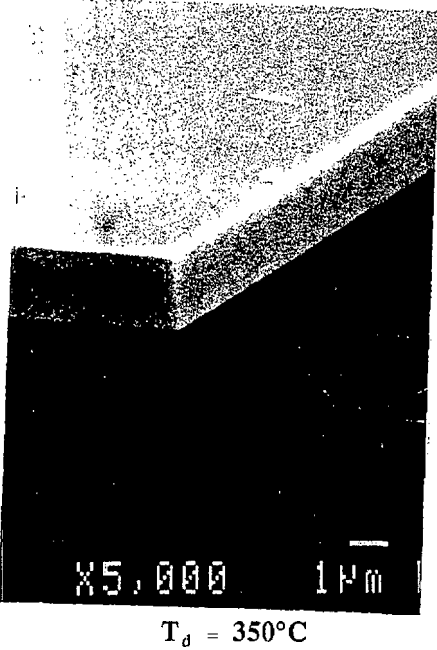
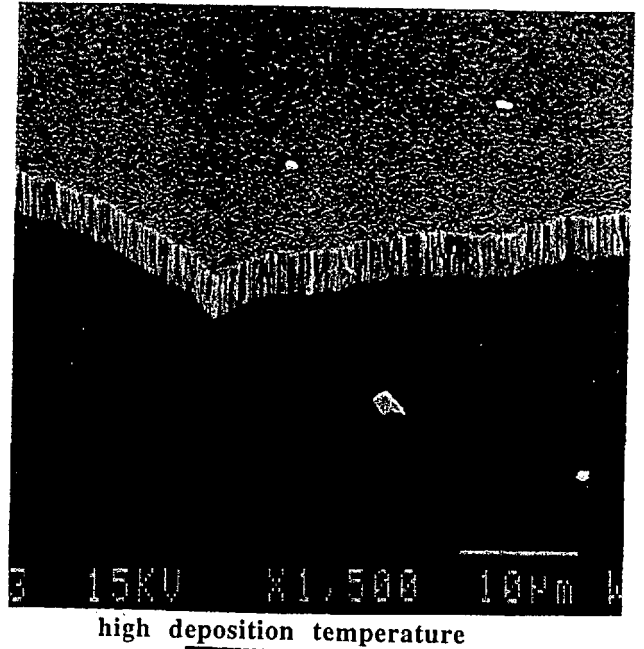
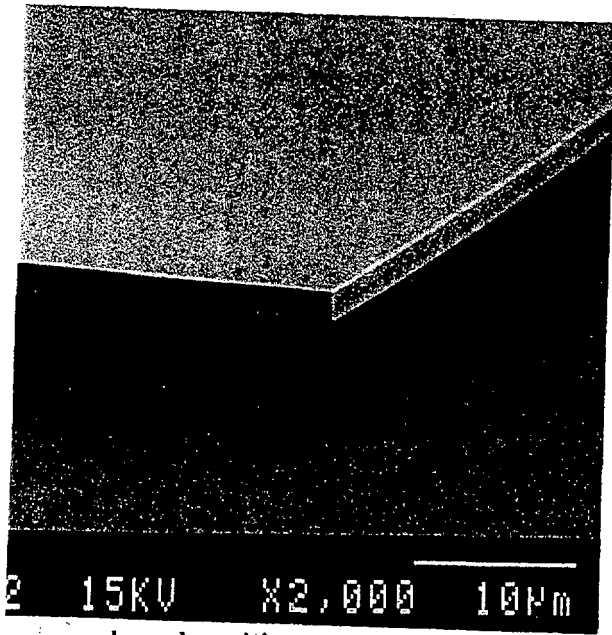


Figure 2: S.E.M. micrographs of C.V.D. films

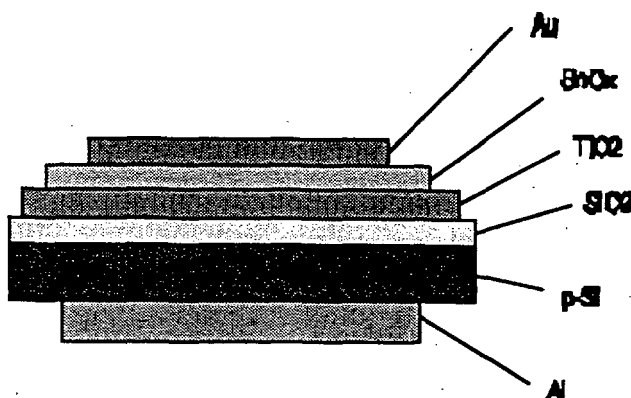
CHAPTER 2: SENSOR CHARACTERIZATION

1. DIODE SENSORS.

1.1 Fabrication of SIS diodes with SnO_x and ITO gates.

Figure 3: Schematic structure of the prepared diodes.

Figure 3 shows the schematic structure of the SIS diodes fabricated. The TiO_2 layer was added in order to improve the insulator properties, since leakage currents were observed at diodes without the TiO_2 layer. This effect was attributed to the thickness of the silicon oxide layer (typical value 85 Å) which was considered inadequate for the elimination of the leakage effects, particularly at relatively high temperatures. It was decided to enhance the insulator layer by e-beam evaporation of TiO_x instead. The deposition of a TiO_x layer was considered suitable for one more reason: to avoid undesirable drifts of the I-V and C-V characteristics of the device at relatively high temperatures.



The TiO_x evaporation was realized using a TiO_x pellet in the electron beam gun boat. Since TiO_x dissociates at the very high temperatures generated by the electron beam, a subsequent furnace oxidation was required (350 °C for 3 hours) in order to compensate for the dissociation. The e-beam evaporation of TiO_x was performed at a pressure of 6×10^{-6} mbar and deposition time was 120 sec. The resulting insulator was transparent in visible light so that it was possible to be measured by the ellipsometric method. The thicknesses of the as deposited TiO_x films were between 300-700 Å, depending on their position in the e-beam gun chamber, as well as on the history of the particular pellet (since TiO_x transforms to $\text{Ti} + \text{TiO}_x$ with time and Ti has a higher evaporation rate).

The fabrication of SIS diodes was performed on oxidized p-type silicon wafers (ellipsometrically measured with thickness of $\text{SiO}_2 = 85$ Å). Evaporation of Al (3000 Å) provided ohmic contacts on the Si surface. Deposition of SnO_x or ITO (as the sensing layer) was performed by reactive magnetron sputtering in order to provide a gate on the TiO_2 surface. Deposition of Au (3000 Å) for ohmic contact was performed by thermal evaporation on the SnO_x or ITO film.

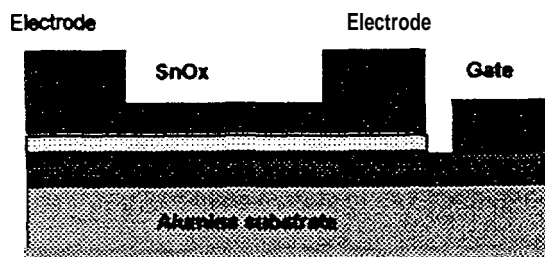
The produced diodes had excellent mechanical properties. The gate material was reactively sputtered at a substrate temperature of 550 °C (partial diffusion of aluminum into silicon also takes place at that temperature, ensuring ohmic contact between Al and Si).

2. VOLTAGE CONTROLLED SENSITIVITY IN MIS STRUCTURES.

2.1 Fabrication of MIS devices.

Figure 4: Schematic structure of the MIS device.

A platinum layer was deposited onto an alumina substrate (gate electrode). An insulating layer was subsequently deposited on the platinum film. The sensing layer (tin or iridium oxide) was reactively sputtered with the aid of an appropriate mask on the insulating layer. There was no electrical contact between the platinum layer and the sensing layer. Gold contacts were deposited on the metallic layer and the two edges of the sensing layer. A voltage difference imposed between the one edge of the sensing layer and the metallic layer served as a bias to modulate the channel width of the sensing layer, as shown in fig. 4. In this way a FET-type voltage controlled resistance was fabricated, with the gate voltage controlling the channel depletion width.



3. A NEW PLANAR DEVICE BASED ON SEEBECK EFFECT.

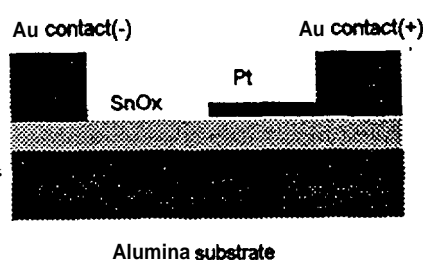
A comparative study concerning the response of tin and iridium oxide thin sputtered films to different reducing gases is presented. The operation of the sensors is based on the seebeck effect. Platinum has been deposited on the half of the films; thus as the rates of gas reaction on the two halves of the films are expected to be different (inducing a temperature gradient), a seebeck voltage is developed as the response signal. Different responses experimentally observed for tin and iridium oxide sensors are qualitatively explained with the aid of the well established theory of chemisorption of reducing gases on metal oxides and the different electronic properties of tin and iridium oxide films. The target gases used were 2000 ppm CO, 10000 ppm CH₄ and 26 ppm C₂H₅OH diluted in Zero Grade Air (ZGA).

3.1 Fabrication of Seebeck effect devices.

Figure 5: Schematic diagram of the seebeck effect device.

SnO_x and InO_x films were deposited with reactive magnetron sputtering on alumina (96%) substrates with dimensions 12x26 mm. Oxygen flow during sputtering was controlled with a Plasma Emission Monitoring apparatus, providing controllable stoichiometry of the deposited film and reproducible films. Oxide thickness was 1000 nm after a 10 min sputtering time.

Platinum was electron-beam evaporated at ambient temperature on the half of the film with an average thickness of a few nm. Gold contacts were subsequently thermally

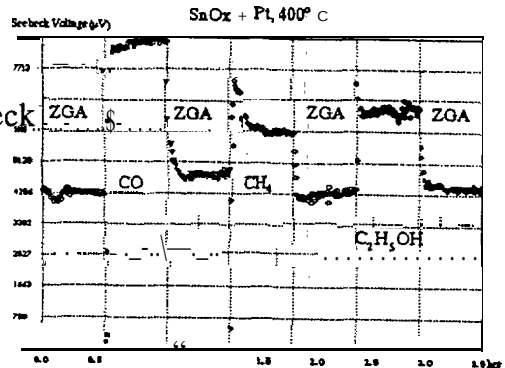


evaporated on the two edges of the substrate. The structure of the sensors is shown in fig. 8.

The sensor characterization setup was designed to measure the steady-state and transient response voltage of the sensors, testing them at constant temperature (provided by an external heater) and under different gases. Sensors were tested at 2000 ppm CO, 10000 ppm CH₄ and 26 ppm C₂H₅OH diluted in zero grade air (ZGA). The sensors were kept at an elevated temperature with the use of an external heater, in order for the chemisorption reactions necessary for sensor operation to take place.

3.2 Response of the seebeck effect device to gases of interest.

Figure 6: Response of tin oxide seebeck device.



CHAPTER 3: PROTOTYPE CHARACTERIZATION

3.1 PROTOTYPE PRODUCTION

The sensor lay-out consists of a 2" x 2" alumina substrate (figure 7a) with 16 sensors in order to develop an industrial process for mass production. The sensors are obtained after laser cutting (figure 7b). For electrical contacts, two different processes were developed: one for the thick SnO₂ films prepared by IMEC (figure 7d) and one for the thin SnO₂ films prepared by ARMINES (figure 7c). The reason is the difference of the thickness between the thick films generally used as electrical contact and the thin SnO₂ films used as sensing material in the latter case.

In the first batch electrical measurements were not possible on a major part of the thin film structures' (80%) because of defects on the gold thin films. The origin of these problems was investigated and was due to misalignment of masks during the printing processing, scratches and evaporation of the gold film during laser cutting.

To solve the -problem an extra run was realized by IMEC and CORECI. These new sensor structures were tested and they still presented some problems: for this batch there was no problem of adjustment at IMEC but the gold thin films showed always scratches and holes. Only 20% substrates have been considered as "good" substrates.

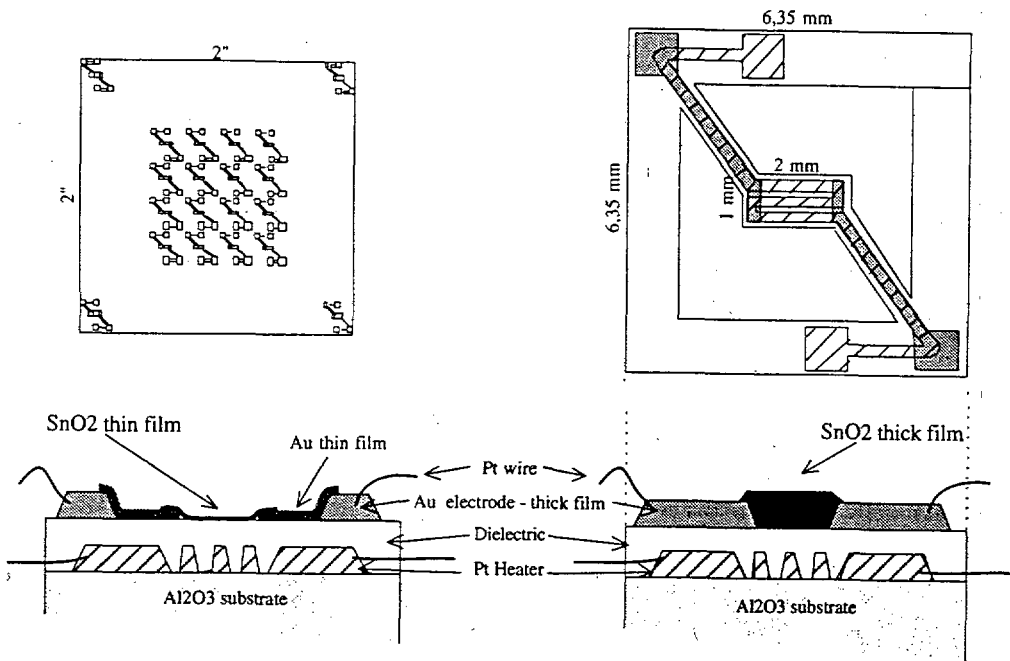


Figure 40: sensor prototypes: a) alumina substrate with 16 sensors; b) details of sensor with the heating area (1 x 2 mm); c) electrical contacts for thin films; d) electrical contact for thick films.

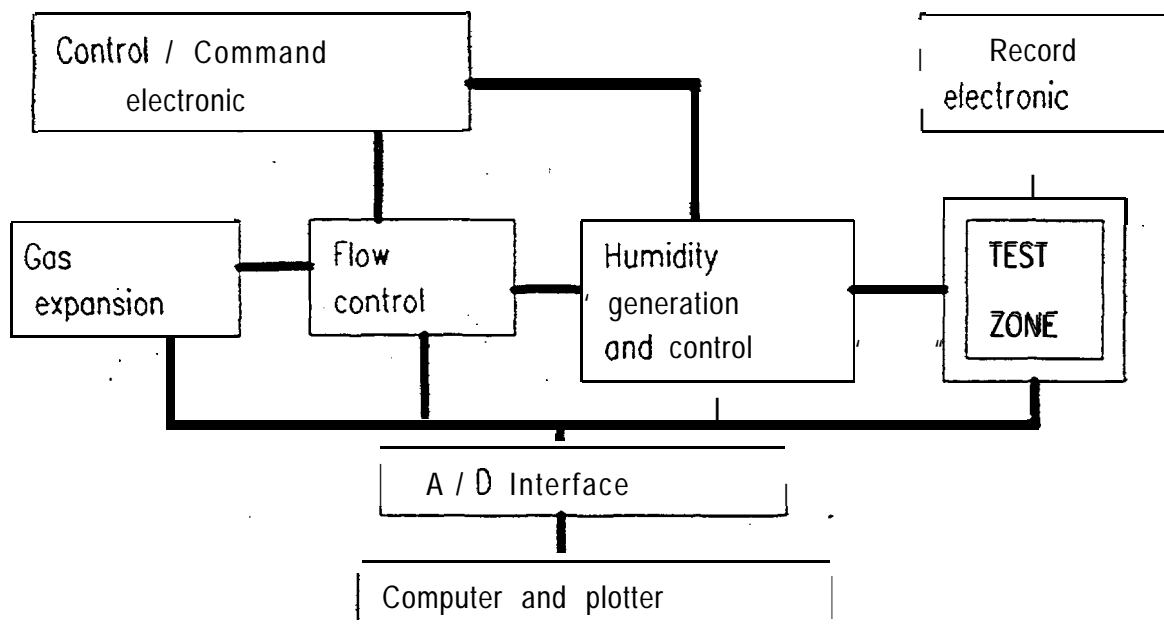
3.2 FUNCTIONAL PROTOTYPE

3.2.1 Test set up@ sensor characterisation

In order to realise all the tests specified in the sensor specification? CORECI developed a test equipment in order to characterise the samples delivered by other partners. According to the type of gas to be tested, the apparatus can generate simultaneously or alone CH₄, CO or alcohol in the interesting range of concentration.

10 Sensors could be tested simultaneously. These sensors were placed in an individual thermocontrolled glass cell. The relative humidity and the temperature (respectively in the range 0 to 90 %RH and 5 to 90° C) in the test zone are monitored. The gasflow of each cell is also controlled with the flow meter.

As far as the electronic part of the testing system is concerned, each sensor is capable of working individually isothermally or by temperature scanning. The testing system can monitor all the data from the sensors and from the other apparatus such as relative humidity transmitter, controllers or indicators.



Test set up for chemical sensors

3.2.2 .Sensor specification

From the proposal of CENELEC Technical Committee TC116 following sensor specification were used in the DEMOST project:

<u>Response time</u>	typical	maximum
for CH ₄ and LPG	5-10 sec	20 sec at 25% of LEL

Low response to Ethanol:

relation between signal to 1000 ppm of Ethanol and 1000ppm of LPG
 optimum 1 to >10
 typical 1 to 3
 tolerable 1 to 1.5
 critical 1 to 1 or < 1

Poison resistance (as defined by CENELEC)

N02 15 ppm for 1 h	Loss of sensitivity against LPG within the standard
S025 ppr ⁿ for 1 h	Loss of sensitivity against LPG within the standard
HMDS 10 ppm for 2 h	Loss of sensitivity against LPG within the standard

Measurement of 100% LEL signals:

For a correct characterization of a sensor it is necessary to measure the gas response in steps of 10% LEL up to 100% LEL
 In order to avoid the dangerous high concentrations, the response curve is measured between 0 and 60% of LEL, and the 100% value is approximated by a linear extrapolation.

Sensor testing:

Based on the sensor specification as described above, the sensors are characterized under methane, N butane and propane as target gases and under ethanol, NO₂, SO₂ and HMDS as interfering gases.

The sensors have been exposed to the gases in a concentration range from 0 to 60% of LEL. This results in :

methane: 0 to 30000 ppm v

N butane: 0 to 8400 ppm v

propane :0 to 12000 ppm v

Other parameters are:

RH : 50%

ambient temperature in the cell 23°C

flow rate 0.25 l/min

pressure: 101000 Pa

measurement voltage 2.5 V

All results are expressed in G/G_0 in Siemens, where G_0 is the value of the conductance under fresh air and G the conductance under gases or interfering gas.

For each gas, following test procedure has been applied:

1) Time response measurement

From 0 to 25 % LEL at 90 % of the full response

Alarm test at 25% LEL

2) Isothermal calibration at 450 °C from 0 to 60 % of LEL

3) Temperature--and humidity influence "at 10% and 25 % of LEL

4) Relation between the conductivity under 1000 ppm of ethanol and 1000 ppm of LPG

5) Doping effect and influence of NO₂ after the sample is exposed to 15 ppm of NO₂ for 1 hour

6) Doping effect and influence of SO₂ after the sample is exposed to 5 ppm of SO₂ for 1 hour

7) Doping effect and influence of HMDS after exposure to 10 ppm of HMDS for 2 hours

Final results:

Sensor types	Supplier	Number tested
Demost 7	IMEC	100
Demost 20	IMEC	100
Demost 7 + SO ₂	IMEC	1
Demost 20 + SO ₂	IMEC	1
In ₂ O ₃ + Pt	NTUA	20
In ₂ O ₃	NTUA	2

The response curve is measured between 0 and 60 % of LEL, the 100% value is estimated by linear approximation

The **metallo-organic** based sensors showed no significant sensitivity against the target gases. For that reason and also for health reasons (M-O materials were forbidden in Belgium during this project) metallo-organic inks were not taken in consideration in the project.

From the first batch of thick film sensor which were investigated it became clear that the doping effect on all sensors after exposure to S02 and HMDS were to high. In order to reduce these effects, new samples were pretreated with S02 according to a procedure which was used successfully for pressed /sintered SnO2 material, such that the doping effects of S02 should be minimized.

V. CONCLUSIONS

Following conclusions, compared to the original objectives, can be made :

- SnO₂ is the most promising material as gas sensing material;
- Thin (sputtering, evaporation, CVD) as well as thick film technology can be used to produce gas sensing films;
- The different fabrication processes,with process parameters and the resulting gassensitivity is determined;
- It was demonstrated within the project that these sensors could easily be produced on lab scale;
- The required mechanics and. electronics for a prototype apparatus for field test was realised;
- The extra technical specifications put forward in the CENELEC working group on gas detection in domestic application were not met in the project. This was also confirmed by the initial field test results.

As such immediate commercialisation of the sensors developed in the DEMOST project will not occur. Extra treatments for stabilizing the sensor response as well as to diminish the interference of some poisoning effect are known to the consortium. It was therefor thought that the implementation of these treatments could be done in a rather. small time period, which was the motivation to formulate a request for extention of the project for 5 months. This however was to optimistic and the implementation of such treatments on films would require a 2 year effort.

ANNEX 1 : LIST OF PUBLICATIONS

1. Reactive sputtering process model for symmetrical planar diode systems, J.N. Avaritsiotis and C.D. Tsiogas, THIN SOLID FILMS 209 (1992), pp. 17-25
2. A model for reactive magnetron sputtering, C. D. Tsiogas and J.N. Avaritsiotis, VACUUM 43(3) (1992), pp.203-211.
3. Modeling reactive sputtering process in symmetrical planar de magnetron systems, C.D. Tsiogas and J.N. Avaritsiotis, JOURNAL OF APPLIED PHYSICS, 7 1(10) (1992), pp.5173-5182.
4. Monte carlo simulation of high rate reactive sputtering of tin oxide in planar dc magnetron systems, C.D. Tsiogas and J.N. Avaritsiotis, THIN SOLID FILMS 219 (1 992), pp.270-277.
5. Transient effects of tin oxide co sensors in the presence of water vapour, D.S. Vlachos, P.D. Skafidas and J.N. Avaritsiotis, APPLIED PHYSICS LETTERS 63(27) (1993), pp.1760-1.
6. Simulation of reactive sputtering from concentric dual-source magnetron in roll to roll coating process, C.D. Tsiogas and J.N. Avaritsiotis, VACUUM 45(4) (1.994), pp.473-481.
7. Modelling and simulation of tin oxide based thick-film gas sensors using monte carlo techniques, P.D. Skafidas, D. S. Vlachos and J. N. Avaritsiotis, SENSORS AND ACTUATORS B18-19 (1994), pp.724-728.
8. Modelling and simulation of abnormal behaviour of thick film tin oxide gas sensors in CO, P.D. Skafidas, D. S. Vlachos and J. N. Avaritsiotis, SENSORS AND ACTUATORS B21 (2) (1994), pp109-121.
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