Sensors & Transducers, Vol. 257, Issue 3, May 2022, pp. 20-29

www.sensorsportal.com

Sensors & Transducers

Published by IFSA Publishing, S. L., 2022
http://www.sensorsportal.com

Doping of Nanocrystalline SnO_2 for High Sensitivity Resistivity Sensors to Detect H_2S (g) in Air

[1,2, *] Mariana P. Poiasina, [2] Mario F. Bianchetti, [2]Eduardo Heredia, [2] Horacio Canepa and [2] Noemi E. Walsöe de Reca

[1] Jorge Sabato Institute, CNEA-UNSAM, San Martín, Prov. Bs As, Argentina
[2] DEINSO-CITEDEF (UNIDEF-MINDEF-CONICET), Juan Bautista de La Salle 4387 (B1603ALO). Villa Martelli, Prov. Bs. As, Argentina
[1] Tel.: (+54 11) 4709-8100
E-mail: mppoiasina@gmail.com

Received: 25 April 2022 /Accepted: 27 May 2022 /Published: 31 May 2022

Abstract: In this work, several factors to increase the sensitivity of a high precision resistive type sensor able to detect from (10 to 15) ppm de H_2S (g) in air, are considered. It is accepted that the doping of the material sensor (SnO_2) increases the dispositive sensibility. Several dopants were proved, concluding that the CuO was the most convenient. Several papers are found in the bibliography presenting different techniques to dope the material sensor but, in this work, an own developed at DEINSO technique was employed, in which the dopant is homogeneously distributed in the SnO_2 crystalline lattice. At first, it was proposed to dope the nanocrystalline SnO_2 with different CuO concentrations (1 %wt. 5 %wt. and 6 %wt.) to choose the most convenient one, which resulted 5 % wt. CuO. Under these conditions, a more sensible sensor was built and other factors were studied to increase even more the sensitivity. The 5 %wt CuO-SnO_2 was deposited on thin films (or layers) forming a multilayers system (which employed from three to six layers or superimposed thin films). The sensor material was characterized with different techniques, such as: DRX, SEM-EDS and GISAXS, which enabled to determine the mean crystallite size, the multilayer system thickness, the crystallinity, the chemical composition and the layers porosity. With the built sensor, (10 to 15) ppm of H_2S (g) in air concentration was measured at an operation temperature (T_o) of 140 ºC. This finding enabled to solve the request of an ambiance security sensor for the oil cracking plant of an important Argentine oil company.

The following subject is not included in this paper but, it is interesting to inform that higher sensitivity of the same described sensor it was possible to detect concentrations from (4 - 5) ppm of H_2S (g) in air at T_o=~ 30 ºC, which makes possible to build a medical use sensor to detect H_2S (g) very low concentrations (minor than 5ppm) which are found in halitosis of hepatic maladies.

Keywords: High sensitivity sensor to detect sulphide gas, Nanocrystalline SnO_2, CuO doped SnO_2, Thin films multilayered system, Sensing mechanisms.

1. Introduction

SnO_2 is an n semiconductor which is frequently employed to build resistive type sensors to detect low concentrations of toxic or explosive gases, among them: CO, VOCs, H_2, NO_x and H_2S.

Hydrogen Sulphide (H_2S) is an extremely toxic gas, even in very low concentrations mainly if they are aspired for a long time. H_2S (g) may be produced in natural processes, among others: from volcanic gases, natural gas, stagnant water and by organic materials decomposition or by an artificial way being produced

in chemical industries, research laboratories, industrials plants, among others. In every case, the early monitoring and detection of the H_2S (g) in air results of the highest importance to guarantee the human security and sensors constitute the main way of identifying and to monitoring the detection levels.

In the oil industry, the oil extraction, refinement and cracking activities are affected by the exposition to H_2S (g), since this gas is found in the oil crudes in their own oil fields [1, 2]. The control international organisms the Occupational Safety and Health Administration (OSHA) EE.UU., The National Institute for Occupational Safety and Health (NIOSH) de EE.UU., the American Conference for Governmental Industrial Hygienists (ACGIH), among others, have established for their laboratories and plants, where the H_2S (g) is produced, an exposition limit to the gas in an 8 hours-working day of: (10-15) ppm of H_2S (g) in air. The Argentine Legislation (Resolution 295/03) also stablished as a permission of maximal measured in time concentration (CMP) and a maximal permissible concentration in short time periods (CMP-CPT) a value of (10-15) ppm of H_2S (g) in air, respectively [3, 4, 5]. Consequently, the authors´ interest is focused in developing high sensitivity sensors to detect (10-15) ppm of H_2S (g) in air, which is in accord with the required conditions for the requested sensor by the oil cracking plant.

DEINSO-UNIDEF-CITEDEF research group is devoted from more of two decades to the study and development of resistive gas sensors using SnO_2 as the sensor material of toxic and explosive gases built with thick and thin films. The DEINSO previous experience enabled to demonstrate that sensors built with nanocrystalline materials reached a higher sensibility (33-37%) in comparison with sensors which were built with the same material though microcrystalline. Otherwise, the optimal operation temperature (T_o) range decreased from (360-450) °C to (180-200) °C and even to minor temperature ranges according with the work conditions, for example: in case of employing nanocrystalline SnO_2 instead of polycrystalline SnO_2 [6, 7].

The SnO_2 functionality as gas sensor is due to its composition and microstructure and to the surface catalytic activity. The SnO_2 doping with metallic atoms or metallic oxides, both aggregated in low concentrations, constitute a theme to be considered, which not only modify the electrical response of the sensor layer but also is able to modify its microstructure. Bibliography points out that the H_2S (g) sensitivity and selectivity increase of a built with SnO_2 sensor was got doping the SnO_2 with a basic oxide, particularly CuO. The authors consulted several papers proving that in the CuO-SnO_2 system, the CuO particles are dispersed in SnO2 acting as the only receiver of H_2S (g), enabling to increase the sensor selectivity to the gas but, in that stage, it was never possible to detect (10 - 15) ppm of H_2S (g) in air as requested for the high sensibility sensor [8, 9, 10]. In the mentioned papers it is informed that systems were built in which the dopant is not homogeneously distributed in the whole SnO_2 nanocrystalline matrix because they were built from oxide powders mixtures or from CuO coating on the SnO_2 or by diffusion putting Cu layers on the SnO_2 [8, 9, 10]. In these cases, it results very difficult to arrive to a homogeneous dopant distribution.

In this work, a doping different method is informed, as based in a sol-gel synthesis, through which it is possible to obtain doped with CuO, nanocrystalline SnO_2 with the included CuO in the SnO_2 crystalline lattice. With this material, the thin film sensor was built and the multilayers system was obtained with the superimposed thin layers. The sensor was characterized with different techniques and the system high sensibility to H_2S (g) was proved as well as the built sensor low operation temperature (T_o).

2. Experimental

2.1. Doping and Synthesis

High purity chemical reagents were necessary to synthesize and to dope the sensible material. For the coating of the superimposed thin films a dip-coating equipment, which was built in our laboratory: DEINSO-UNIDEF-CITEDEF was employed [11].

As a synthesis method, the sol-gel technique was employed. Sol-gel is a chemical synthesis way able to get complex materials departing from chemical precursors which are simpler in their structure. Departing from the alcoholic solution of a salt (which contains the metallic cation of interest, Sn^{+2} in this case, it is possible to obtain coatings with a reticular structure. The process consists in preparing a precursor solution of $SnCl_2.2H_2O$ in absolute ethanol and in introducing it in a hot bath with constant agitation. During heating, hydrolysis reactions occur, enabling to form a colloidal suspension of solid particles in a liquid medium (sol). Simultaneously, a polycondensation occurs, long molecular chains are formed, which are surrounded by solvent, generating a reticular structure and constituting the gel. Afterwards, through an adequate thermal treatment, the corresponding metallic oxide is formed maintaining the reticular structure of precursor [12]. Then, a doping proceeding by sol-gel was developed. This doping way shows advantages in comparison to classical doping techniques, by example: the impregnation doping, by powders mixture or by CuO diffusion in the SnO_2. The material is formed from a Cu^{+2} /Sn^{+2} solution enabling the thin layers where the CuO and the SnO_2 are forming part of the same homogenous lattice which is doped with a determined proportion (5 wt% CuO).

The laboratory work enabled to find the optimal experimental conditions which, with the performed characterisations enabled in two technical methods to discard one of them. The experimental variants were identified as MCuI and MCuII techniques:

I. MCuI technique: consists in preparing a 0.5M $SnCl_2.2H_2O$ solution in absolute ethanol, aggregating a weight percent solution of $CuCl_2.2H_2O$ (dopant) which is placed in a thermostated bath at (80-100) °C with constant agitation till obtaining a transparent solution.

II. MCuII technique: it is prepared a 0.5M $SnCl_2.2H_2O$ solution in absolute ethanol. The solution is agitated till a whole dissolution, obtaining a transparent and crystalline liquid. It is placed in a thermostated bath at (80-100) ºC with agitation. It is aggregated to the solution a corresponding a weight percentage of $CuCl_2.2H_2O$. It is important to slowly aggregate the salt at T_{amb} with constant agitation till obtaining a colourless and transparent solution.

Both, obtained MCuI and MCuII solutions were deposited by dip-coating, on a glass substrate, building a multilayers system (with three superimposed layers), the thermal treatment of each layer (or thin film) was slowly performed with a slow heating, from Tamb till 400 ºC maintaining the temperature to reach the molecular precursor, causing the SnO_2 doping.

2.2. Characterization Techniques

To study the properties of the obtained layers, they were characterized using the X Rays Diffraction (XRD) technique, in a Pananalytical, difractometer, Empyrean model with a PIXCEL3D detector, belonging to the Physics Department-belonging to the National Atomic Energy Commission-CNEA; Scanning Electron Microscopy (SEM) together with X Rays Energy Dispersion (EDS) performed 1) with a Philips SEM, 505 model, belonging to National Institute of Industrial Technology-INTI and 2) with a SEM Carl Zeiss, NTSupra 40, belonging to Centre of Advanced Microscopies-CAM,FACEN- Buenos Aires University-UBA; Low Angle X Rays Difraction with Grazing Incidence-GISAXS, with a Xenocs 2.0 Xeuss equipment, with a Pilatus detector to get images, Applied Crystallography Laboratory, belonging to the San Martin National University-UNSAM.

Materials crystallinity was studied by XRD and crystallites mean size was calculated applying the Scherrer equation. With SEM, it was observed in layers, the surface state and homogeneity and the multilayers system mean thickness, as formed by three superimposed layers, was measured. The semiquantitative chemical analysis of layers was performed with EDS with the Electronic Microsonde included in the SEM. GISAXS enabled to evaluate the sensitivity and the sensor optimal operation temperature, measurements of sensor electrical resistance were performed as the sensor was exposed to H_2S (g) in air low concentrations. Employing the GISAXS technique, it was also possible to study the surface aspect proving if the surface was completely smooth or presenting porosity which is produced by physisorption [13]. It was then possible, to determine the thin layers porosity and to measure the mean pores size and their dispersion.

In gas sensors, which are built with SnO_2 as base material, usually being resistive type sensors, adsorption reactions occur between the air oxygen adsorbates (O^-, O_2^-, O^{2-}) and the grains surface of SnO_2. When this state is reached, an increase of potential barrier in the grain boundaries (GB) due to the electronic exchange between SnO_2 and the absorbates is produced. When the sensor is in contact with a reducing gas, it reacts with absorbates liberating them from the SnO_2 surface, restoring the electrons to the material volume and producing, in consequence, a decrease of the potential barrier, decreasing the materials electrical resistance. This change of electrical resistance is proportional to the reducing gas quantity and it is the sensor measuring parameter. Sensitivity (S) is defined as (1):

$$S = R_{air}/R_{air+gas}\ , \tag{1}$$

where R_{air} is the material electrical resistance which is exposed to pure air and $R_{air+gas}$ is the electrical resistance if the material is exposed to a gas/air mixture.

3. Results

To study the different proposed concentrations of dopant it was found a higher sensitivity in doped with 5 wt% CuO sensors (Fig. 1). The specimens were treated by the techniques: MCuI or MCuII. The SEM images show a smooth and homogeneous surface for MCuI type specimen (Fig. 2a). The EDS analysis confirms that copper is homogeneously distributed in the whole surface (Fig. 2b). But, in MCuII type specimen, crystalline clusters are observed (Fig. 3). With EDS it was confirmed that the agglomerated crystals in clusters contained Cu, which was not homogeneously distributed in the crystalline SnO_2 lattice (Fig. 4). The substrate corresponding to MCuI type specimen were cut to observe the profile to determine the thickness of the multilayer system (Fig. 5). The average thickness value of several multilayers systems, all them composed of three superimposed layers, resulted of (230 ± 1.0) nm.

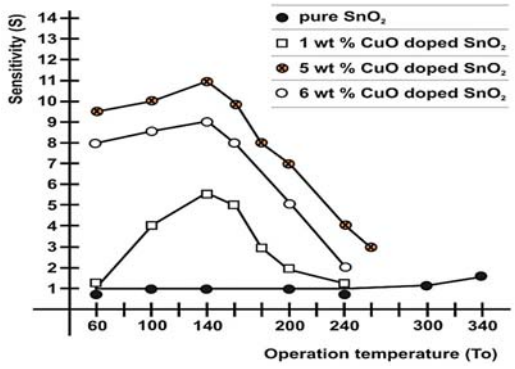

Fig. 1. Sensitivity (S) vs operation temperature (T_o) for different CuO concentrations (1 %wt, 5 %wt and 6 %wt). The highest sensitivity corresponds to SnO_2 doped with 5 %wt CuO.

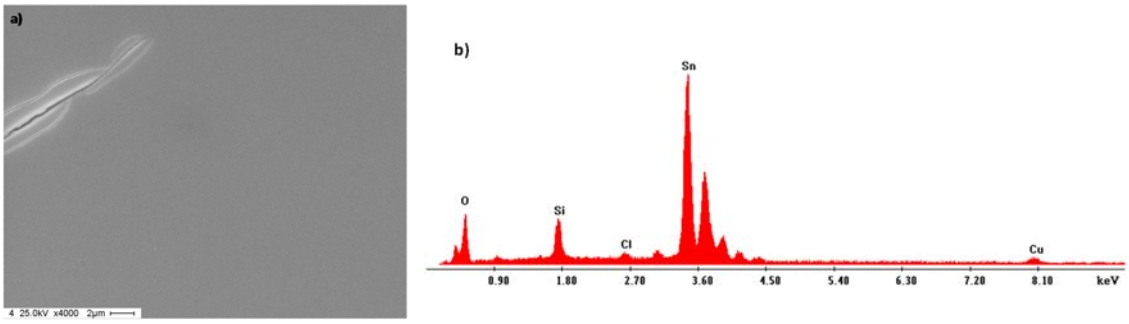

Fig. 2. a) SEM (4000x). Surface image of a MCuI specimen; b) EDS analysis showing the presence of Sn and Cu in the layer.

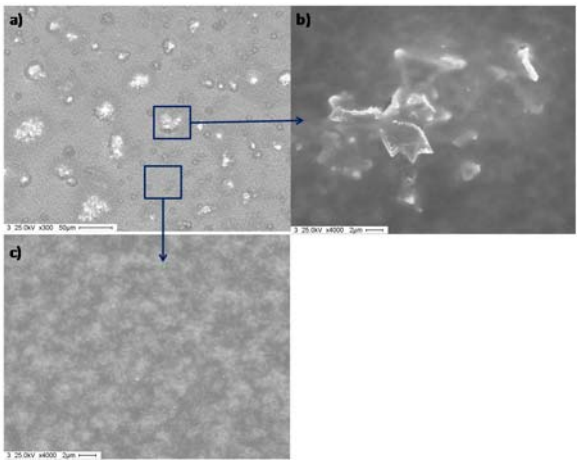

Fig. 3. SEM images, micrographies of MCuII specimen. a) A non-homogeneous surface is observed with clusters of crystals; b) Magnification of a crystals cluster. c) Magnification of a zone free of crystalline agglomerations.

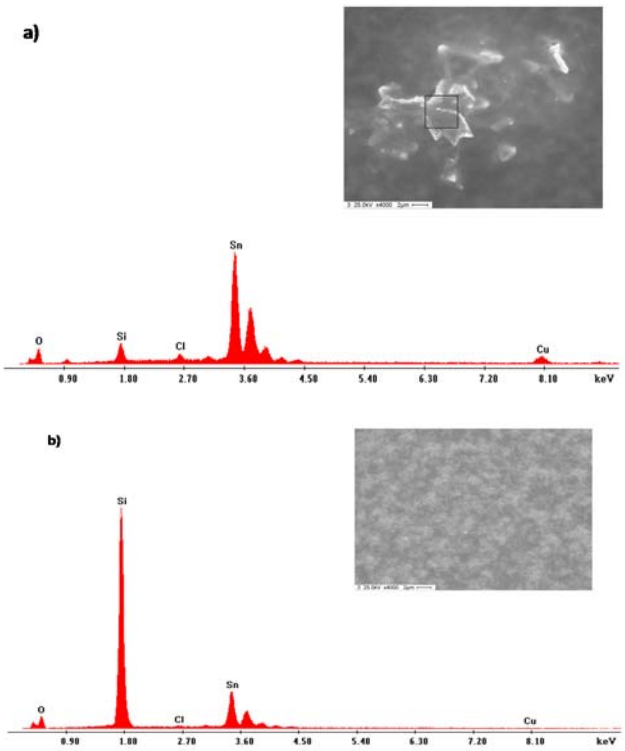

Fig. 4. a) EDS analysis of agglomerated crystals corresponding to a very low CuO concentration (1 %wt). It is observed a mayor Sn presence, while Cu is in very low proportion; b) EDS analysis of the free of crystalline clusters zone, where not Cu was detected.

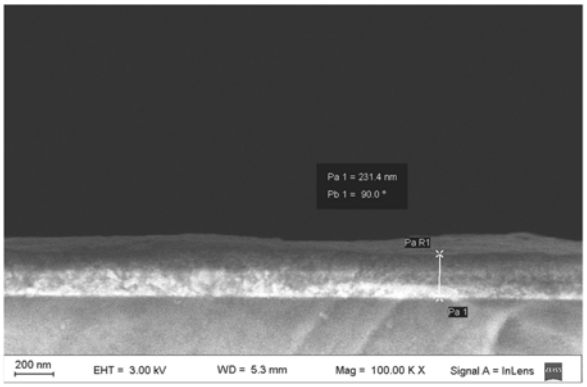

Fig. 5. SEM (100.000x). Micrography in which a mean thickness (230±1.0) nm is measured in a multilayer system. The multilayers system is formed by three superimposed layers deposited by dip-coating, the whole thickness is shown in the graph with a white arrow.

With the X Rays diagram (DRX) it was recognized the tetragonal rutile phase of pure SnO_2 (Fig. 6) in the MCuI specimen. The CuO was not detected because of its low concentration (5wt%) which is under the method detection limit.

The crystallite mean size was calculated by the Scherrer equation (2):

$$D_{sch} = \frac{k\lambda}{\beta \cos\theta}, \quad (2)$$

where k is the constant (usually taken as 0.94), λ is the wave length of the X rays beam, β is the whole width taken in half of the maximal high (FWHM) of a given peak (after the elimination of the instrumental widening as measured in radians) and θ is the peak diffracted angle (in radians).

In Table 1 the obtained results are presented.

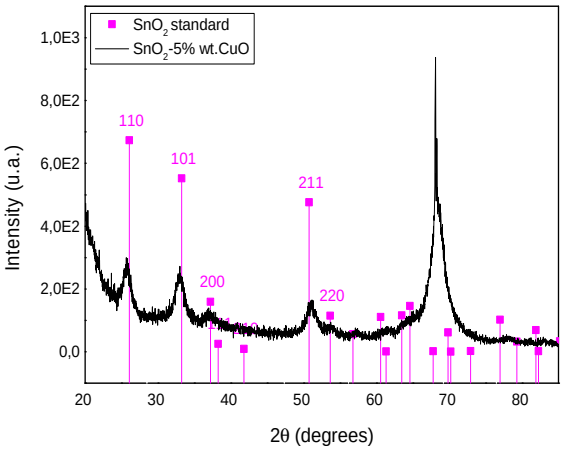

Fig. 6. DRX results of a MCuI specimen corresponding to a doped 5 wt%CuO-SnO_2 multilayers system.

By GISAXS the layers porosity was studied. Three different MCuI type specimens were analyzed and the number of deposited layers was varied. The MCul type specimens were obtained by sol-gel and dip-coating in 2, 4 and 6 superimposed layers (multilayers) on a glass substrate (Table 2).

Table 1. FWHM (°) obtained values, (°) is: each peak position and Dsch is the thin layers calculated value for doped 5 wt% CuO SnO_2.

Peaks Ner	k	λ (nm)	2θ (°)	β (°)	D_{sch} (nm)
1	0.94	0.15418	26.59491	0.97647	8.26949 ± 0.14231
2	0.94	0.15418	33.8907	1.13307	7.004972 ± 0.23334
3	0.94	0.15418	37.20549	1.44423	5.445017 ± 0.07394
4	0.4	015418	51.93453	1.02631	7.268469 ± 0.39724
D_{sch} of doped SnO_2 = (6.99 ± 0.21) nm					

Table 2. Characteristics of the analysed by GISAXS Specimens.

Specimen Type	Synthesis Technique	Coating Technique	Layers Number	Substrate Type
M4	sol-gel	dip-coating	4	glass
M5	sol-gel	dip-coating	2	glass
M6	sol-gel	dip-coating	6	glass

A mean radius pore value resulted between 1.5 nm and 2.5 nm. It is not considered significative the effect of the deposited layers number on their porosity. It was found that the pores exhibited a revolution ellipsoid form and their relation aspect was calculated: 2.34, 1.98 and 2.74 for M4, M5 y M6, types of samples, respectively. The dispersion in pores radius was also calculated, obtaining the values: 1.77 nm; 1.79 nm and

1.98 nm for the samples of M4, M5 and M6 types, respectively.

Figs. 7, 8 and 9, a) corresponds to the analysed specimens on which information was got from GISAXS diagrams, and b) the experimental dates (dotted line) contrasted with the carried out fitting as performed with the IsGisaxs program (full line). Each colour line corresponds to the gathered data in a horizontal line of GISAXS diagrams.

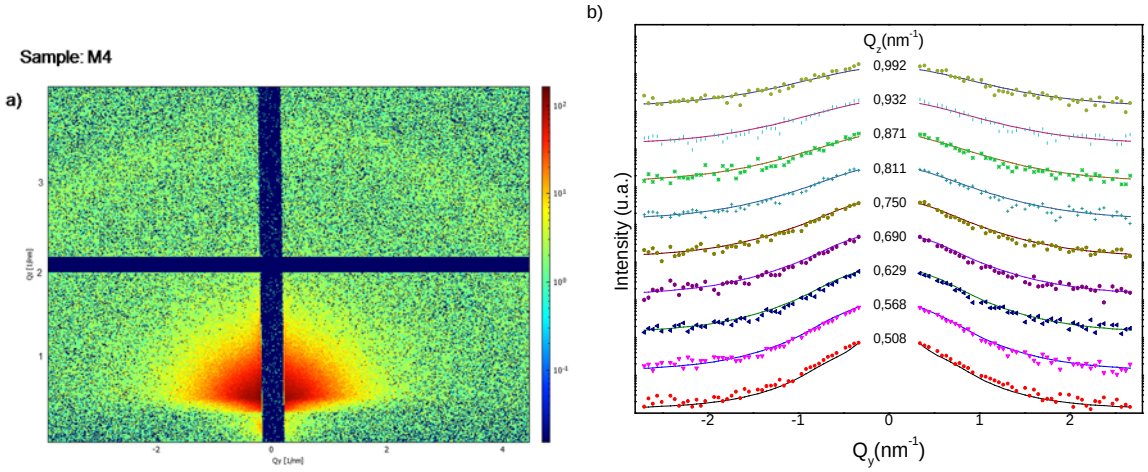

Fig. 7. a) GISAXS diagram. b) Graph in which the experimental data are represented and the fitting line was got by the software for an M4 type specimen.

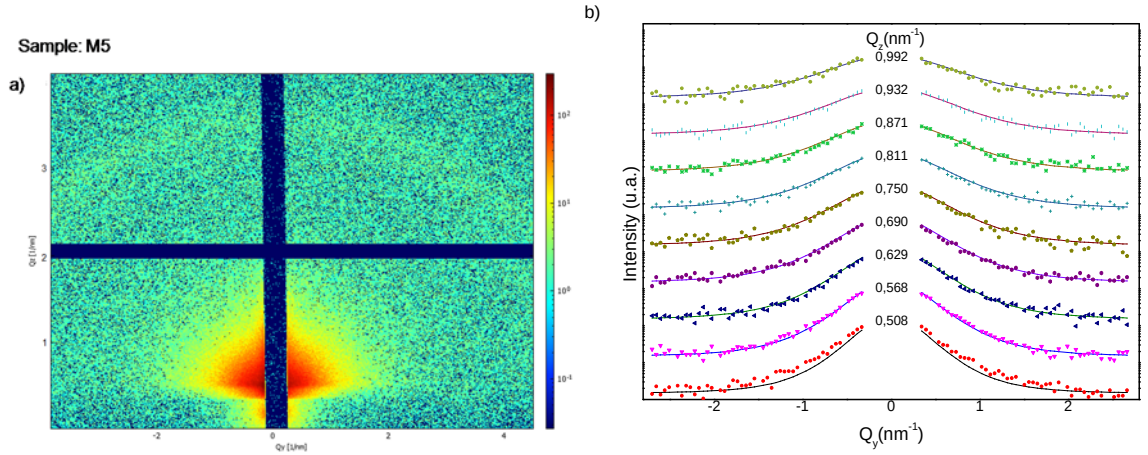

Fig. 8. a) GISAXS diagram. b) Graph in which the experimental data are represented and the fitting line is got by the software for an M5 type specimen.

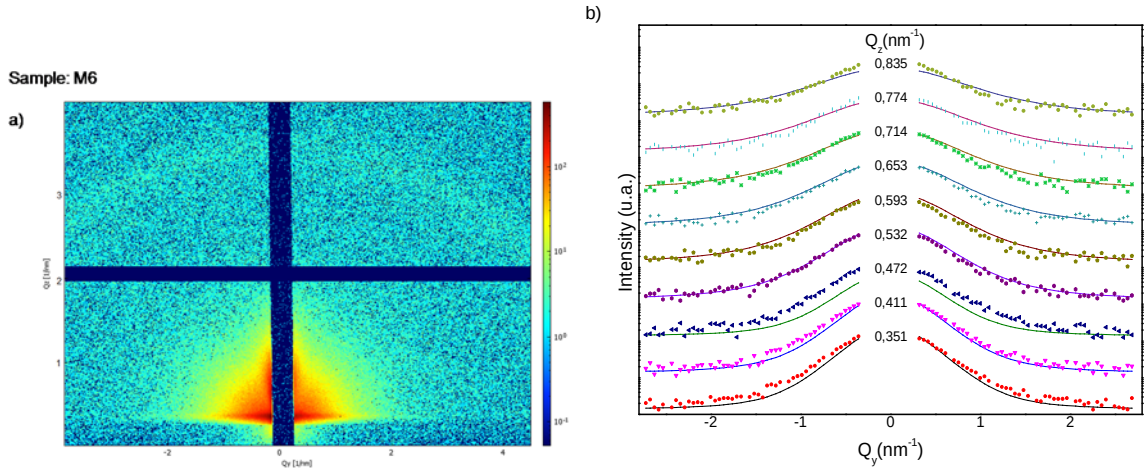

Fig. 9. a) GISAXS diagram **b)** Graph in which the experimental data are represented and the fitting line was got by the software for a M6 type specimen.

The statistics to calculate the pores mean radios and their dispersion, was made with the logNormal method (Fig. 10). In Table 3, the obtained results are presented.

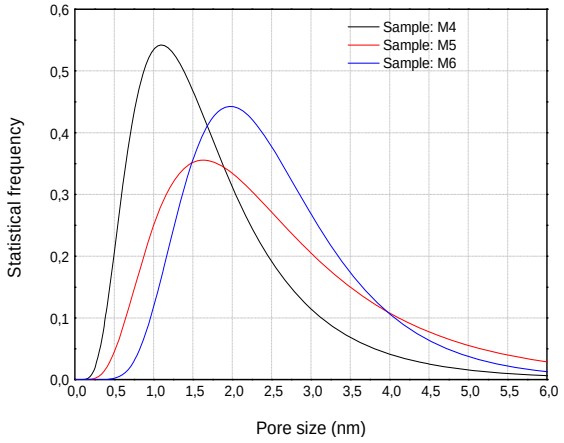

Fig. 10. Graph in which the correspondence between the pores mean radius and statistic frequency are represented for the M4, M5 and M6 type specimens.

Table 3. Got results of pore mean radius, the dispersion and pores aspect relation corresponding to the analysed specimens.

Specimen Type	Pores mean Radius (nm)	Radius Dispersion (nm)	Aspect Relation (height/radius)
M4	1.52	1.77	2.34
M5	2.29	1.79	1.98
M6	2.35	1.98	2.74

With the got results it was possible to conclude that the pores mean radius in all the specimens, was found between 1.5 nm and 2.5 nm. It was not found an important change in the pores radium in pure and doped (with low dopant concentrations, i.e.: doping with 5 wt% CuO). This doping is considered the ideal one to produce a mayor sensor sensitivity.

The system to measure the sensors sensitivity was designed in our laboratory and it is constituted by a precision current Keithley 220 source and a Keithley model 6517B electrometer to measure the electrical resistance in function of the gas in air concentration.

The gases dosage is performed with an Atmega328 microcontroller which operates the gas commutation electrovalves to commute: aire/aire+gas and the caudal mass regulators with which the gaseous mixture is controlled. The same microcontroller realizes the temporization of the electrometer data capture.

The air/air+gas fluxes and the sensor are thermostated in the measurement zone by a heating sheet and is feed with a PID regulator which is based in another Atmega328 microcontroller.

The obtained data are stored in a PC to be processed. The software was developed in our laboratory and it is continuously updated to adapt it to the needs and changes which could be produced in the system.

The specimen electrical contacts are made with low temperature silver painting, with a thermal treatment at 120 ºC for 15 min, in order to evaporate the whole painting and not enabling the evaporation of the whole painting solvent in order to avoid its interference in measurements.

To observe in a graphic way the changes in the electrical resistance, cycles were assembled in which the synthetic air circulation and the H_2S gas (diluted in synthetic air at different concentrations) are commuted. Once the specimen is at the desired operation temperature, synthetic air is circulated to clean the circuit and then, the gases commutation cycles begin while the tension fall is measured between the contacts.

The electrical measurements in thin (5wt% CuO SnO_2) layers prepared with the MCuI technique and with the MCuII technique (Table 4).

Table 4. Specimens details in which the electrical resistance changes when they are in H_2S (g) in air presence.

Sensor Specimen	Sensor Material Concentration	Doping Technique	Thin Film Coating	Substrate Type
MCuI	5 wt% CuO SnO_2	CuI	dip-coating 3 layers	glass
MCuII	5 wt% CuO SnO_2	CuII	dip-coating 3 layers	glass

The optimal operation temperature (T_o) was 140 ºC for both, MCuI and MCuII specimens (Fig. 11). The relative sensitivity (Sr) of MCuI specimens resulted considerably mayor than that of the MCuII specimens (Fig. 12). These results point out that MCul is a better material as sensor for H_2S (g) in air in very low concentrations.

It was studied the electrical resistance variation of MCul specimens when they were exposed to 10 ppm of H_2S (g) in air at T_o = 140 ºC (Fig. 13) confirming that it was the optimal sensor.

Fig. 14 Graph of electrical resistance in function of time for two sensors, exposed to air/gas cycles at 140 ºC: a) a sensor built with pure SnO_2 (without

doping) and b) a sensor built with doped SnO_2 (with 5 wt% CuO).

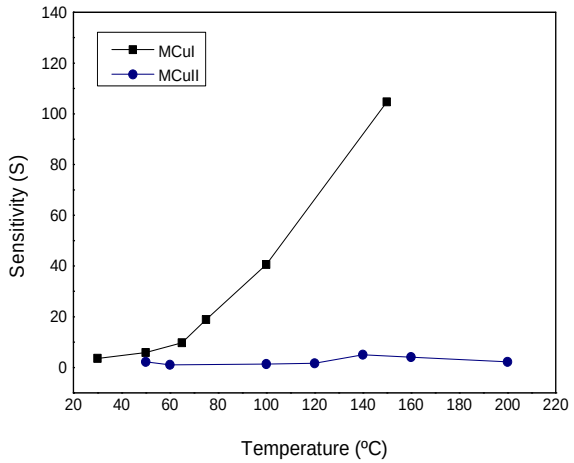

Fig. 11. Sensitivity graphs of a MCuI and a MCuII specimens vs the operation temperature.

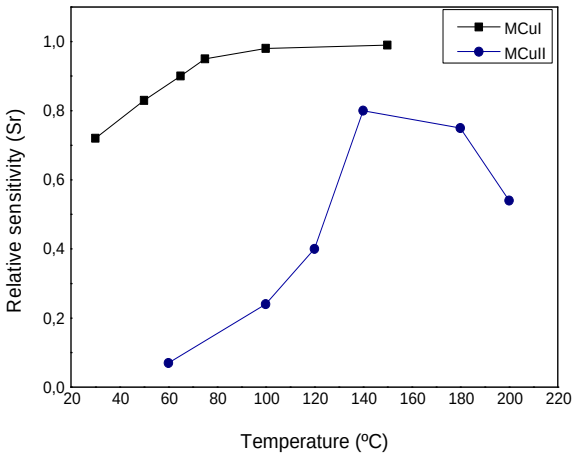

Fig. 12. Relative sensitivity (Sr) vs the operation temperature for the MCuI y MCuII specimens.

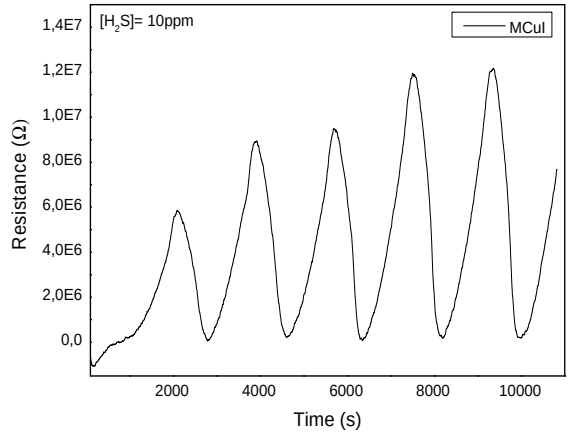

Fig. 13. Electrical resistance change of MCuI sensor which was exposed to 10 ppm of H_2S (g) in air, at T_o= 140 ºC.

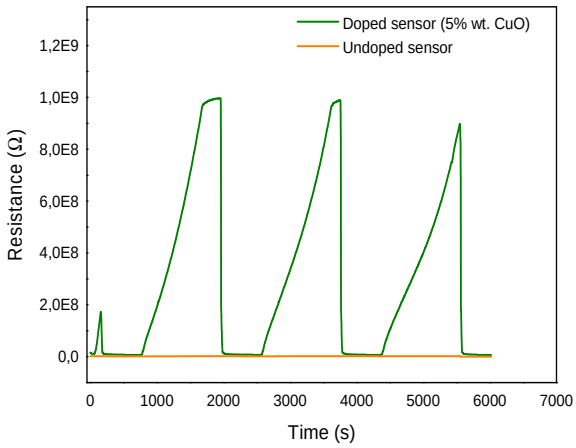

Fig. 14. Graph of electrical resistance vs time for air/gas cycles at 140 ºC, of two sensors to measure H_2S (g) in air. a) Sensor built with pure SnO_2 (without doping); b) A sensor built with doped 5wt%CuO SnO_2.

4. Discussion

With respect to the functioning of a sensor detecting low concentrations (ppm) of H_2S (g) in air, it is necessary to previously consider the dispositive building. The sensor material (SnO_2) presents a crystalline and homogeneously doped structure with a considerably low percentage of CuO. In this case, it was concluded that the most convenient CuO proportion, as homogeneously contained in the SnO_2 structure was 5 wt% CuO. After doping no changes in the doped SnO_2 could be observed and the initial tetragonal crystallographic rutile structure was conserved.

Bibliography gathers several common processes to dope SnO_2 [8, 9, 10] as performed by diffusion (consisting in CuO or pure Cu layers intercalation) leaving them to diffuse in the SnO_2 layers, taking always into account the conservation of CuO proportion. Mixtures of both oxides were also deposited. In many of these processes, a CuO in SnO_2 lattice inhomogeneous distribution was observed. In case of material for sensors built in this way, the proposed mechanism still accepted is described in [14]. The authors propose that the non stoichiometric CuO_x (**p** type semiconductor) and the SnO_{2-x} (n type semi-conductor) exhibit a strong electronic interaction due to the numerous p-n joints causing a very high resistance of films in air. In contact with the reducing H_2S (g) gas, the CuO is sulfurized according with the equation (3), breaking the p-n joints and decreasing the sensor electrical resistance. That electrical resistance is the sensor measuring parameter:

$$CuO + H_2S \rightarrow CuS + H_2O \quad (3)$$

After the exposition to O_2, CuS is oxidized once again according to the equation (4):

$$CuS + 3/2\ O_2 \rightarrow CuO + SO_2 \quad (4)$$

Several papers consider this theme in the bibliography, among them [16-18]. It is interesting the A. Khana et al´ paper [16] in which the thin layers were prepared by a simultaneous thermal evaporation of Sn and Cu, also assuring the homogeneous distribution of dopant.

Experimental conditions in this work, resulted quite different from those which were as cited in every previous paper, since in this case, the two oxides are mixed forming a homogeneous system as it was before informed.

With regards to the gas diffusion model in the multilayers system (built at DEINSO-UNIDEF-CITEDEF) is simple and geometric and it employs (as before informed) from three to six superimposed CuO-SnO_2, layers as observed in the model of Fig. 15. The H_2S (g) diffuses on the doped SnO_2 surface and through short circuits like grain boundaries, dislocations, vacancies clusters or holes. During diffusion, in the thermally activated processes, the gas is in contact with the external surface and easily distributed on it, migrating to the inner of system through the short circuits (pores, dislocations or grain boundaries [17].

The gas finds interfaces which separate two layers or two adjacent thin layers. The interfaces show dislocations which were caused by non-epitaxial contacts between contacting layers. In another partial contacts between deformed neighbouring layers (for example by tensions), holes could be found which, sometimes, are clustered facilitating the gas diffusion. This type of defects, may act as vacancies clusters in diffusion. In Fig. 15, the different types of defects are gathered in a simple model which was described in a previous work [7]. Besides, if the coating technique such as dip-coating is employed to deposit the thin layers also tensions may be generated and the defects density may also increase. In order to understand the defects density in a normal or augmented concentrations, in these fundamental situations it is necessary to simulate the diffusion-reaction processes and the system sensing mechanism.

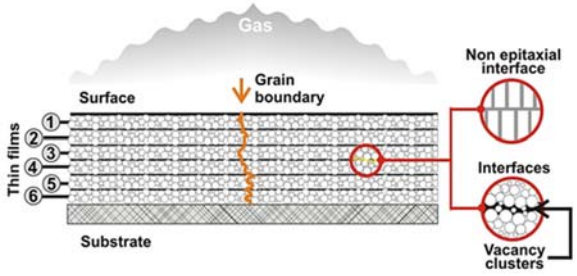

Fig. 15: Simple model of the multilayers system with the found different defects.

Define abbreviations and acronyms the first time they are used in the text, even after they have been defined in the abstract. Abbreviations such as IEEE, IFSA, ac, dc, ms, etc. do not have to be defined. Do not use abbreviations in the title or heads unless they are unavoidable.

5. Conclusions

It was demonstrated as based on the got sensitivity results that in the built sensor, several factors exist which contribute to reach a high sensitivity, one of them is the use nanocrystalline materials. Nanomaterials show a mayor surface/volume relation that the one of microcrystalline materials. This fact enables a mayor contact surface between the sensitive material and the gas, then increasing the sensor sensitivity. Otherwise, according to Yamazoe´ model [8], an inversely proportional relation between the sensitivity and crystallite size appears. Using the synthesis techniques by sol-gel and dip-coating, under the specified work conditions, a material with a very low crystallite size was got resulting in an optimal size of: (6.99 ± 0.21) nm.

An important factor in the sensitivity augment and these sensors selectivity is the doping method. The authors have reported the doping technique as based in sol-gel and dip-coating. It was demonstrated that, this material shows a mayor sensitivity in comparison with different doping techniques [8-10], this fact is due to the obtained nanocrystalline homogeneous material, in which the dopant is included in the SnO_2 crystalline lattice.

As it was mentioned in the discussion, the sensor design in multilayers together the thin layers tensions, appearing in thin layers during the coating and thermal treatments generate tensions and defects which are able to accelerate the gas diffusion through the material, augmenting the dispositive sensitivity.

With all the mentioned factors as the crystallite size, the doping method (to-day with a patent in process) and the diffusion which is accelerated through the defects and multilayers tensions is possible to explain the obtained sensor high sensitivity being able to detect (10-15) ppm of H_2S (g) in air, at an operation temperature (T_o) of 140 ºC and with the possibility of decreasing even more the detection limit and the and the operation (T_o) temperature, as it was previously informed in this work.

References

[1] Nicholas P., Cheremisinoff P. and Rosenfeld P., Handbook of Pollution Prevention and Cleaner Production - Best Practices in The Petroleum Industry, *William Andrew Publishing*, 2009.

[2] Valdez Salas B., Schorr Wiener M., Carrillo Beltrán M., Ramos Irigoyen R., Curiel Alvarez M., Materiales and Corrosion in Natural Gas Industry. Valdez Salas B. & Schorr Wiener M. (Eds.) and Corrosion and Preservation of the Industrial Infrastructure, *OmniaScience*, Barcelona, Spain, 2013, pp. 87-102.

[3] OSHA Web Portal (https://www.osha.gov/hydrogen-sulfide)

[4] NIOSH Web Portal (https://www.cdc.gov/spanish/niosh/npgsp/npgd0337-sp.html) (In Spanish)
[5] It corresponds to the Argentine Legislation Web Portal (http://www.argentina.gob.ar/normativa/nacional/resoluci%C3%B3n-295-2003-90396/texto) (in Spanish)
[6] Bianchetti M. F., M. P. Poiasina and Walsöe de Reca, N. E. Patent in procedure on: Thick Film Sensor to sense Hydrogen built with nanostructured pure Tin Oxide, *P20130101354*, applied on 11/04/2018.
[7] M. P. Poiasina, C. L. Arrieta (DEA-CITEDEF), M. F. Bianchetti y N. E. Walsöe de Reca, Resistive thick and thin Film Gas Sensors built with Nanomaterials and related Research, in Advances in Sensors: Reviews, Vol. 6, Chapter 1, *IFSA Publishing*, Spain, 2018, pp. 1-37.
[8] J. Tamaki, T. Maekawa, N. Miura, N. Yamazoe, CuO-SnO_2 Element for highly sensitive and selective Detection of H_2S, *Sensors and Actuators B*, 9, 1992, pp. 197-203.
[9] J. Liu, X. Huang, W. Liu, Z. Jiao, W. Chao, Z. Zhou, Z. Yu, H_2S Detection Sensing Characteristic of CuO / SnO_2 Sensor, *Sensors*, 3, 2003, pp. 110-118.
[10] A. Ayesh, A. Alyafei, R. Anjum, R. Mohamed, M. Buharb, B. Salah, M. El-Muraikhi, Production of sensitive Gas Sensors using CuO / SnO_2 Nanoparticles, *Applied Physics A*, 125, 2019, 550.
[11] M. F. Bianchetti and Bravo H., Dip-coating Equipment, DEINSO-UNIDEF-CITEDEF Index Card Ner. 887/ISSN 0325-1527, 2016.
[12] C. J. Brinker and G. W. Scherer, Sol-Gel Science - The Physics and Chemistry of Sol- Gel Processing, *Academic Press Inc*., Boston, 1990.
[13] M. Thommes, K. Kaneko, A. Neimark. J. P. Oliver and Rodriguez-Reynoso, Physisorption of Gases, with Special Reference to the Evaluation Surface Area and Pore size Distribution. IUPAC Technical Report, *Pure and Appl. Chem.,* 87, 9-10, 2015, pp. 1051-1069.
[14] G. S. Devi, S. Manorama y V.J. Rao, High Sensitivity and Selectivity of a SnO_2 Sensor to H_2S around 100 ºC. *Sensors & Actuators, B-Chemical,* 28, 1995, pp. 31-37.
[15] S. Manorama, G. S. Devi, J. V. Rao, Hydrogen Sulfide Sensor based on Tin Oxide deposited by Spray Pyrolysis and Microwave Plasma chemical Vapor Deposition, *Appl. Phys. Letters,* 64, 1994, pp. 3163- 3168.
[16] A. Khana, R. Kumar, S. Bhatti, CuO-doped SnO_2 thin Films as Hydrogen Sulphide Gas Sensor, *Appl. Phys. Letters,* 82, 24, 2003, pp. 4388-4390.
[17] H. Lu, W. Ma and J. Gao, Diffusion-reaction Theory for Conductance Response in Metal Oxide Gas Sensing thin Films, *Sensors & Actuators, B-Chemical,* 66, 2000, pp. 228-231.
[18] N. Matsunaga, G. Sakai, K. Shimanoe and N. Yamazoe, Diffusion Equation basic Study of thin Film Semiconductor Gas Sensor-Response Transient, *Sensors & Actuators, B-Chemical,* 83, 2002, pp. 216-221.
