



**HAL**  
open science

## Thickness effect on VOC sensing properties of sprayed In 2 S 3 films

R. Souissi, N. Bouguila, B. Bouricha, C. Vázquez-Vázquez, Marc Bendahan,  
A. Labidi

► **To cite this version:**

R. Souissi, N. Bouguila, B. Bouricha, C. Vázquez-Vázquez, Marc Bendahan, et al.. Thickness effect on VOC sensing properties of sprayed In 2 S 3 films. RSC Advances, 2020, 10 (32), pp.18841-18852. 10.1039/d0ra01573c . hal-02867071

**HAL Id: hal-02867071**

**<https://amu.hal.science/hal-02867071>**

Submitted on 24 Mar 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Thickness effect on VOCs sensing properties of sprayed In<sub>2</sub>S<sub>3</sub> films

R. Souissi<sup>a,b</sup>, N. Bouguila<sup>c,\*</sup>, B. Bouricha<sup>b</sup>, C. Vázquez-Vázquez<sup>d</sup>, M. Bendahan<sup>e</sup>, A. Labidi<sup>b,f</sup>

<sup>a</sup>Tunis University, Ecole Nationale Supérieure d'ingénieurs de Tunis (ENSIT), Tunisia.

<sup>b</sup>Carthage University, Laboratoire des Matériaux, Molécules et Applications IPEST, BP 51, La Marsa 2070, Tunis, Tunisia.

<sup>c</sup>Gabès University, Laboratoire de Physique des Matériaux et des Nanomatériaux appliqué à l'environnement, Faculté des Sciences de Gabès, Cité Erriadh, Zrig, 6072 Gabès, Tunisia.

<sup>d</sup>Laboratory of Magnetism and Nanotechnology (NANOMAG), Department of Physical Chemistry, Faculty of Chemistry, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

<sup>e</sup>Aix Marseille Univ, Université de Toulon, CNRS, IM2NP, Marseille, France.

<sup>f</sup>Department of Physics, College of Science and Arts at Ar-Rass, Qassim University, P.O. Box 1162-Buraydah 52571, Saudi Arabia.

## Abstract

This work reports the thickness effect on the sensing performances of In<sub>2</sub>S<sub>3</sub> material for some Volatile Organic Compounds (VOCs). In<sub>2</sub>S<sub>3</sub> films were deposited on glass substrates by the spray pyrolysis technique. Different samples were prepared via changing spray time in the range of 10-90 min. The film thickness varies from 0.8 μm to 6.1 μm. The X-ray diffraction results demonstrate that the In<sub>2</sub>S<sub>3</sub> films are polycrystalline in nature and exhibit a cubic structure. Additionally, Scanning Electron Microscopy (SEM) and 3D profilometry examinations show that the surface roughness increases with the rising spray time. On the other side, the oxygen adsorption versus a working temperature was investigated. Sensing measurements with ethanol, methanol and acetone gases were carried out by a dynamic control of the current passing through the sensitive layers. The best sensitivity was obtained for the film matching a 70- min deposit time. An understanding detection mechanism based on the oxidation reaction between reduced vapors and chemisorbed oxygen was confirmed. The selectivity of the sensor was analyzed for several volatile organic compounds (VOCs).

## Key words

In<sub>2</sub>S<sub>3</sub> film; spray pyrolysis; thickness; volatile organic compounds; gas sensor

\*Corresponding author: Nouredine Bouguila (N. Bouguila)

E-mail: bouguila.nour@gmail.com

## 1. Introduction

Volatile organic compounds sensors are used in a wide range of applications such as in human breath analyzers [1], food and fruit ripening monitoring devices. Many studies have recently been devoted to the development of selective and organic vapor sensitive sensors. Among these sensors developed nowadays, we can cite metal oxides including single oxide or multi-oxide structures such as  $\text{LaFeO}_3$  [2],  $\text{ZnCo}_2\text{O}_4$  [3],  $\text{CuFe}_2\text{O}_4/\text{-Fe}_2\text{O}_3$  [4],  $\text{ZnO}$  [5-7],  $\text{SnO}_2$  decorated  $\text{SiO}_2$  [8]. The literature review for the latest achievements has shown some very promising results. Recently, metal sulfides have been studied as a new sensitive class for vapor detection. It has been shown that cadmium sulfide ( $\text{CdS}$ ) films are more sensitive to Ethanol than Cadmium Oxide ( $\text{CdO}$ ) [9]. Nevertheless, these materials are considered toxic. It is therefore important to develop non-toxic films such as Indium Sulfide  $\text{In}_2\text{S}_3$ . Various techniques such as Spray Pyrolysis [10,11], Hydrothermal [12], Ultrasonic Dispersion [13], Chemical Bath Deposition (CBD) [14], Physical Vapor Deposition [15], etc., have been used to prepare  $\text{In}_2\text{S}_3$ . The Spray Pyrolysis method has been chosen in this work. Indeed, this method, which is both simple and not expensive for the deposition of large area thin films, does not require high quality targets or vacuum and is a facile way to dope material by adding a doping element to the spray solution [16]. The physical properties of the obtained  $\text{In}_2\text{S}_3$  films depend on synthesis parameters such as deposit time, substrate temperature and spray solution flow rate [17,18].

$\text{In}_2\text{S}_3$  is an n-type semiconductor of group III-VI with a wide energy band gap ranging from 2 to 3 eV [17-19]. It can exist in four allotropic crystal structures as a function of temperature and pressure [20]. At room temperature and atmospheric pressure,  $\text{In}_2\text{S}_3$  has been found to crystallize into the defective spinel structure  $\beta\text{-In}_2\text{S}_3$ , which is a stable phase and presents many Sulfur vacancies  $V_S$  (donor), Indium vacancies  $V_{\text{In}}$  (acceptor), and Indium interstitials  $I_{\text{In}}$  (donor) in the unit cell [20].

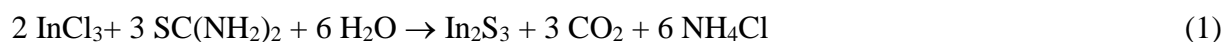
This material shows interesting optoelectronic and semiconductor sensitization properties which allow it to be used as a buffer layer in solar cells [21,22], a heterojunction in photovoltaic electric generators [23-24], biological imaging sensors [25] and a photodetector [26-28]. More recently, Cai et al. [29] have demonstrated that  $\text{In}_2\text{S}_3$  hierarchical microspheres are good candidates for fabricating practical cataluminescence Ammonium Sulfide sensor. In our earlier paper [30], we reported the use of  $\beta\text{-In}_2\text{S}_3$  thin films deposited by the Spray Pyrolysis technology as an Ethanol sensor. We showed that the  $\text{In}_2\text{S}_3$  layers had a fairly good sensitivity to Ethanol. The optimal operating temperature was found to be  $350^\circ\text{C}$ , the best response to 500 ppm Ethanol concentration was 1.7 and the response/recovery times were about 150 s. These results are encouraging to deepen the study for enhancing sensing performances by acting on the synthesis parameters.

The aim of the present study is to investigate the influence of the thickness of sprayed  $\text{In}_2\text{S}_3$  films on the organic vapor-sensing properties. We discuss also in this paper how the oxygen adsorption/desorption phenomenon impacts the detection mechanism of the analyzed gas. The detection properties were generally deduced from DC measurements which provide information in the general sensor behavior.

## **2. Experimental details**

### **2.1. Films preparation**

$\text{In}_2\text{S}_3$  films were deposited by the Spray Pyrolysis technique. Glass substrates were cleaned in Ethanol and rinsed in deionised water. An aqueous solution was made by a mix of Indium Chloride ( $\text{InCl}_3$ ) and Thiourea ( $\text{SC}(\text{NH}_2)_2$ ) with a ratio of S:In = 2. The solution was sprayed at a flow rate of  $2 \text{ mL}\cdot\text{min}^{-1}$  onto  $1 \text{ cm}\times 1 \text{ cm}$  glass substrates at  $340^\circ\text{C}$  within an accuracy of  $\pm 5^\circ\text{C}$ . Nitrogen was used as a carrier gas and the flow rate was kept constant at  $6 \text{ L}\cdot\text{min}^{-1}$ . The deposit time was varied in the range of 10-90 min. The  $\text{In}_2\text{S}_3$  formation results from a global endothermic reaction governed by the following equation [14,18]:



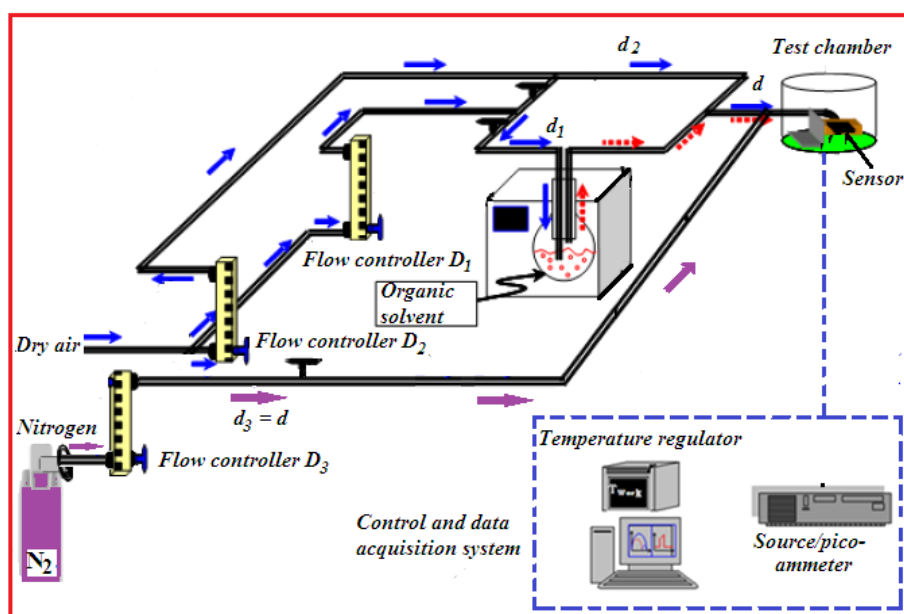
Finally, two rectangular Au electrodes of 5 mm long and 2 mm apart are deposited on the film surface using the Thermal Evaporation technique under high vacuum.

## 2.2. Films characterization

X-ray diffraction (XRD) analyses of the films were performed using monochromatic  $\text{CuK}\alpha_1$  radiation ( $1.54056 \text{ \AA}$ ) (Bruker D8 Advance diffractometer). Topography images and surface roughness were obtained with a non-contact 3D optical profilometer (Sensofar S Neox) in a white-light vertical scanning interferometry (VSI) mode and using a CFI60-2 Nikon objective lens (10x EPI, numerical aperture 0.3 and working distance 17.5 mm). The surface morphology and the chemical analysis were studied by means of scanning electron microscopy (SEM) using a Zeiss Ultra PLUS microscope endowed with an electron dispersive spectrometer (EDS).

## 2.3. Experimental set-up for VOC detection

To investigate gas sensing response, the  $\text{In}_2\text{S}_3$  films were tested using the experimental set-up shown in **Fig. 1**.



**Fig. 1:** Experimental set-up for gas detection.

The global gas circuit has two sub-circuits. The first is used to test the organic vapor generated using two mass- flow controllers D<sub>1</sub> and D<sub>2</sub> which are used to set the dry air flow rate and the organic vapor concentration. The dry air from flow controller D<sub>1</sub> is charged with vapor through a dilution bath containing a pure organic solvent. This latter is maintained at a fixed temperature in order to adjust the saturation vapor partial pressure. This flow is mixed with the second flow of dry air coming from the second flow controller D<sub>2</sub>. By varying d<sub>1</sub> and d<sub>2</sub> (d<sub>1</sub>+d<sub>2</sub> were kept constant at 1 L.min<sup>-1</sup>), diverse concentrations of organic vapor can be obtained and computed using the formula [30,31]:

$$[C](ppm) = \left( \frac{x d_1}{(1+x) d_1 + d_2} \right) \times 10^6 \quad (2)$$

where  $x$  is the molar fraction of the vapor in the bottomed flask at T<sub>vap</sub>, given by:

$$x = \frac{P_{vap}}{P_{atm}} \quad (3)$$

with P<sub>vap</sub> the partial pressure of the vapor at a specified temperature T<sub>vap</sub>, and P<sub>atm</sub> the atmospheric pressure.

The total flow charged with organic vapor has been blown on the sensor for 5 min. Then the test chamber has been purged with dry air for 15 min.

A second sub-circuit is used to check oxygen adsorption/desorption phenomenon. Since the test chamber is dynamic, the gases are controlled at 1 L.min<sup>-1</sup> flow rate. Nitrogen (0% Oxygen atmosphere) is sent along the third arm D<sub>3</sub>. Firstly, the flow loaded with dry air (20% oxygen atmosphere) was sent along the second arm D<sub>2</sub> and blown directly on the sensor for 5 min. Then, it was removed from the test chamber by switching the gas flow to Nitrogen for 15 min.

Samples were polarized at 0.5 V. The measurements of direct current intensity have been done in real time using a (HP 4140B) Source/Picoammeter. The electrical contact on the

sensor is ensured by gold tip tungsten electrodes. Measurements were done at different operating temperatures ranging from 150°C to 425°C. The sensor is heated by a halogen lamp which is powered by a stabilized generator and controlled by an (HP 34401A) Multimeter regulator that allows to set the temperature of the semiconductor by measuring the resistance across the RTD PT100 platinum probe that will be converted into a temperature value.

In order to compare the responses of In<sub>2</sub>S<sub>3</sub> sensors we will use the following formula of sensing response [30,31]:

$$Response = R_a/R_g \quad (4)$$

where R<sub>a</sub> and R<sub>g</sub> represent respectively the sensor resistance value in air and in a sample gas.

### 3. Results and discussion

#### 3.1. Characterization

##### 3.1.1. Thickness and structure

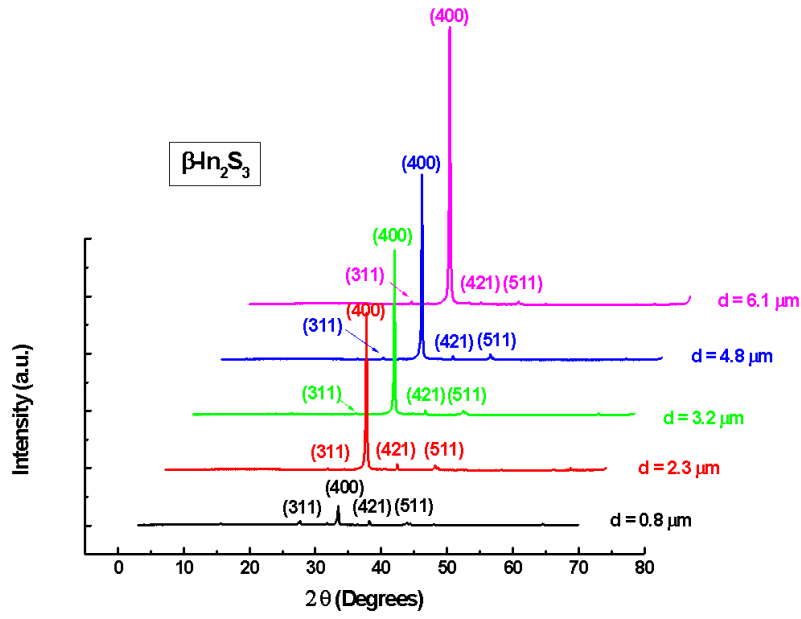
The double weight method was used to measure In<sub>2</sub>S<sub>3</sub> film thicknesses (d) for varying deposit time and calculated by using the relation:

$$d = \frac{m}{\rho S} \quad (5)$$

where *m* is the deposited film mass, *ρ* is the density of the material in the bulk form (*ρ* = 4.613 g.cm<sup>-3</sup> matching with the standard file of JCPDS 25-390) and *S* is the effective area on which the film was deposited.

The obtained values of thicknesses for all samples are illustrated in Table 1 and show that thickness increases from 0.8 μm to 6.1 μm by rising deposit time in the range 10-90 min.

The X-ray diffraction patterns of the In<sub>2</sub>S<sub>3</sub> layers obtained for different thicknesses are shown in **Fig. 2**.



**Fig. 2:** XRD patterns of sprayed  $\text{In}_2\text{S}_3$  films.

These patterns indicate that all films were polycrystalline and can be closely indexed to pure  $\beta\text{-In}_2\text{S}_3$  phase with a simple cubic structure matching with the standard file of JCPDS 32-0456. The preferred orientation observed in the pattern for all samples is (400). The intensity of the diffraction main peak becomes more intense with the increase of spray time. Such behavior can be explained by the increase of film thickness and the increased ability of atoms to orient in proper equilibrium sites giving more preferentially oriented films.

The main peak was used to determine the crystallite size using Lorentzian fits and Scherrer's formula [32]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (6)$$

where  $\lambda$  denotes the wavelength of X-ray,  $\theta$  represents the Bragg angle and  $\beta$  the full width at half maximum (FWHM) in radians.



Likewise, the imperfection in the films can be quantified by computing the dislocation density ( $\delta$ ) which is defined as the length of dislocation lines per unit volume of the crystal. For the (400) peak, it was calculated using the Williamson–Smallman relation [33]:

$$\delta = \frac{1}{D^2} \quad (7)$$

The interplanar d-spacing ( $d_{hkl}$ ) for  $\text{In}_2\text{S}_3$  nanoparticles was calculated using Bragg's equation (8). The lattice parameter ( $a$ ) associated with  $d_{hkl}$  and Miller indices ( $h,k,l$ ) are calculated via the theoretical equations (9) and (10) as well [32]:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta} \quad (8)$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (9)$$

$$a = 4d_{400} \quad (10)$$

The calculated lattice parameter reveals a constant value  $a = 10.7 \text{ \AA}$ , while crystallite size and dislocation density of films are presented in **Table 1**.

Spray time (min)	Thickness ( $\mu\text{m}$ )	D (nm)	$\delta$ ( $10^{10} \text{ lines.cm}^{-2}$ )	Rq (nm)	Rsk
10	0.8	39.1	6.5	141	- 0.35
30	2.3	43.1	5.2	207	- 0.27
50	3.2	51.7	3.7	223	- 0.22
70	4.8	52.1	3.7	501	0.93
90	6.1	41.3	5.8	1150	0.43

**Table 1:** Thickness, data evaluated from X-ray diffraction pattern and roughness profile parameters of  $\text{In}_2\text{S}_3$  films.

It can be seen that the change in thickness affects the density of native imperfections which modify the structural quality of the films. In fact, a maximum of the crystallite size ( $D = 52 \text{ nm}$ ) and a minimum of the defect  $\delta$  ( $\delta = 3.7 \cdot 10^{10} \text{ lines.cm}^{-2}$ ) is located around a thickness of  $4.8 \mu\text{m}$  reflecting the best crystallinity of the deposit in this condition.

### 3.1.2. Topography and morphology

Surface topography is an important surface property and it affects the performance of products at its application fields. Topography of prepared layers was performed by using optical profilometer.

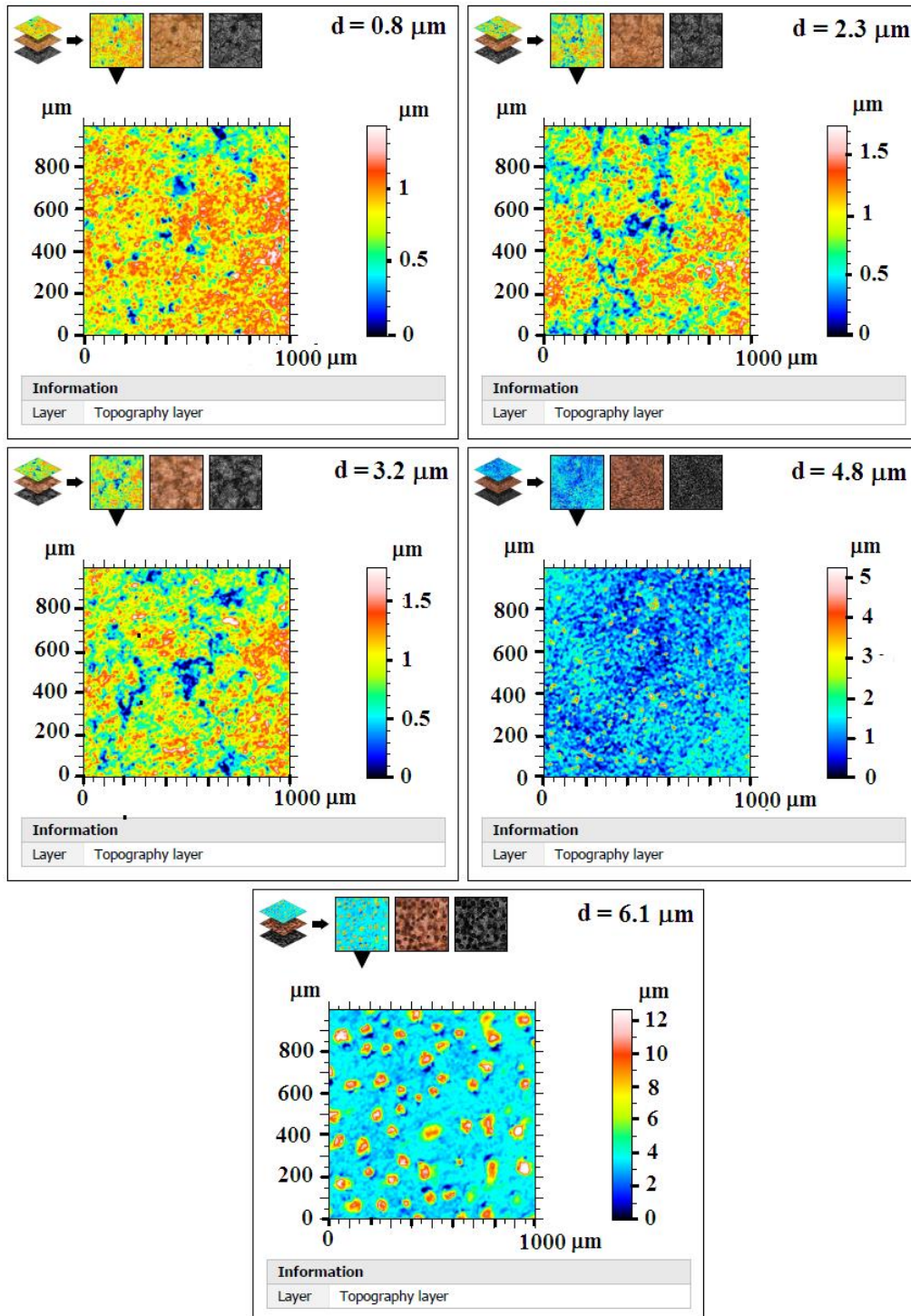


Fig. 3: Topography images of  $\text{In}_2\text{S}_3$  films.

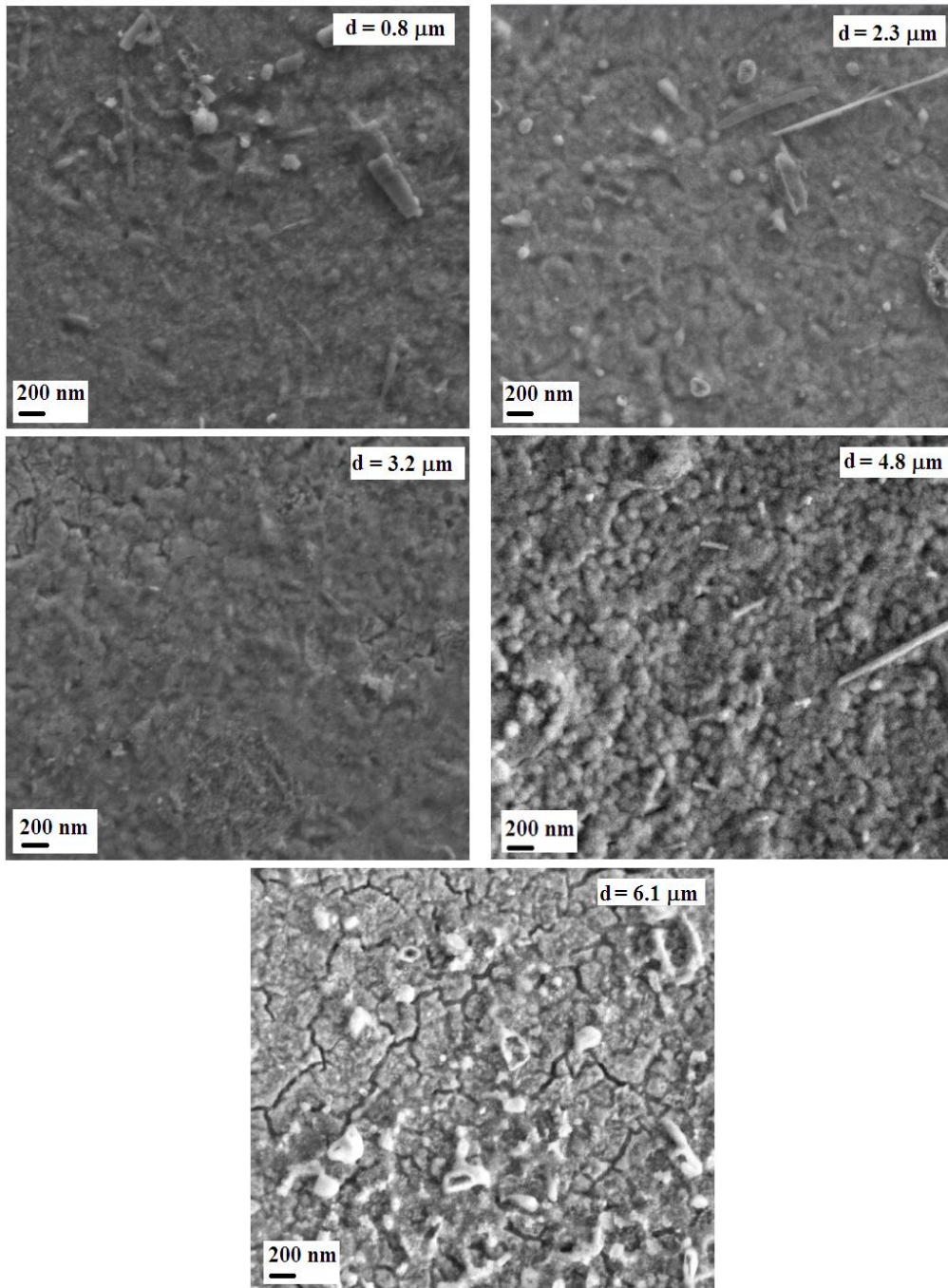
**Fig. 3** presents 2D surface measurement of  $\text{In}_2\text{S}_3$  samples over a scanned area of  $1 \text{ mm}^2$ . In this case we arbitrarily amplify the z axis and we also know the altitudes using a color palette that allows appreciating the local variations of the heights. Here the variations of the relief are also amplified and the represented surfaces would appear flat. The Surface roughness of films seems to change from one layer to another with a changing thickness.

The parameters (prefix) R calculated on the roughness profile are defined in a handful of international standards Geometric Product Specifications (GPS)-Surface Texture: Profile Method (ISO 4287:1997). Some parameters calculated on segments of the profile (the base lengths) and averaged over several segments are presented in **Table 1**. These results are evaluated from measurements in three different areas of each sample and from five profiles for each area.

$R_q$ , root mean squared roughness, is the standard deviation of the height distribution over the evaluation length. We can note from **Table 1** that  $R_q$  increases eventually with increasing thickness by rising spray time and shows high values for samples matching thicknesses of  $4.8 \mu\text{m}$  and  $6.1 \mu\text{m}$ .

$R_{sk}$ , asymmetry of the profile: asymmetry of the distribution of the heights, defined on the length of evaluation. This parameter is important because it gives information on the morphology of the surface state. A positive value of  $R_{sk}$  (thicknesses of  $4.8 \mu\text{m}$  and  $6.1 \mu\text{m}$ ) corresponds to a surface having peaks and protuberances above the surface, and thus a distribution shifts towards the lowest points, while a negative value (thicknesses of  $0.8 \mu\text{m}$ ,  $2.3 \mu\text{m}$  and  $3.2 \mu\text{m}$ ) corresponds to a plateau surface with scratches or deep pores, and a shifted distribution towards the highest points.

The morphological study by SEM shows in **Fig. 4** the microscopic appearance of the surface layers for different thicknesses.



**Fig. 4:** SEM images of sprayed  $\text{In}_2\text{S}_3$  films.

The films were well covered, homogeneous, dense and continuous. We can note that the thickness effect is reflected on the film surface morphologies. SEM images reveal a granular layer for the sample corresponding to the thickness of  $4.8 \mu\text{m}$ , whereas the layers are smooth for the others thicknesses. In addition to this, big granules/chunks are observed at the figure for  $0.8 \mu\text{m}$ ,  $2.3 \mu\text{m}$ , and  $4.8 \mu\text{m}$  thicknesses. Such observation may be a result of a small

deviation from the stoichiometric composition in starting a solution that yields a very strong influence on the microstructure and the surface morphology of the films. This behavior was the subject of previous reports on films such as  $\text{In}_2\text{S}_3$  [34] and  $\text{CuInS}_2$  [35]. We can also note a rougher layer surface with cracks at the higher thickness of 6.1  $\mu\text{m}$  identifying a beginning of crystallinity degradation.

### 3.1.3 Chemical analysis

The use of EDS made chemical elements' identification possible in the obtained thin layers. We report in **Table 2** the counting of the atomic percentage of the main elements in the films.

Thickness ( $\mu\text{m}$ )	S (at.%)	In (at.%)	S/In
<b>0.8</b>	31.60	23.68	1.33
<b>2.3</b>	37.83	30.15	1.25
<b>3.2</b>	37.98	29.90	1.27
<b>4.8</b>	36.92	29.07	1.27
<b>6.1</b>	35.74	28.92	1.24

**Table 2:** EDS results of  $\text{In}_2\text{S}_3$  thin films.

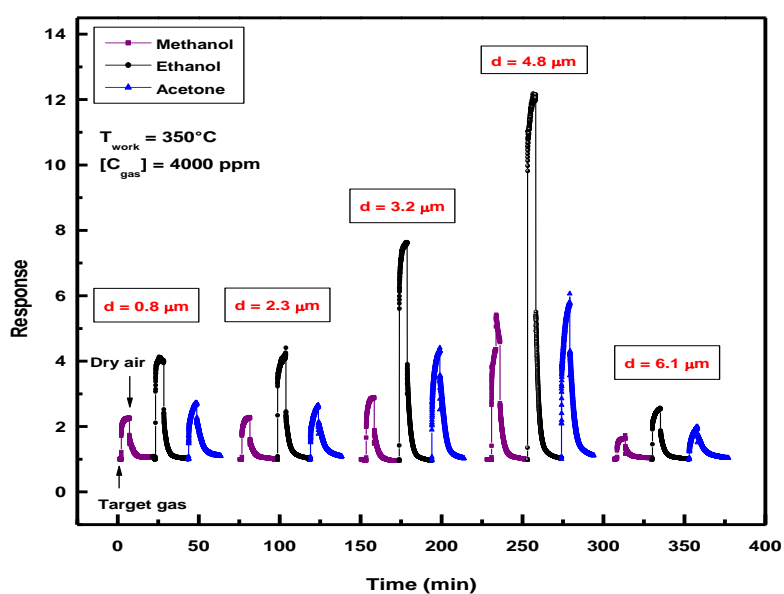
These results are evaluated from measurements in four different areas of each sample. The S/In molar ratio remains constant for all the samples with an average value of 1.27. This order of magnitude is less than the stoichiometric ratio ( $\text{S/In} = 1.5$ ) of the  $\text{In}_2\text{S}_3$  material. This indicates that the prepared  $\text{In}_2\text{S}_3$  material contains defective sulfur positions.

## 3.2 VOCs sensing properties

### 3.2.1 Response

First, all the sensors elaborated with several thicknesses in the range 0.8-6.1  $\mu\text{m}$  were tested to 4000 ppm of Methanol, Ethanol and Acetone gas at an operating temperature of 350°C. The choice of such temperature is based on our previous publication [30]. This is the

optimal temperature for an Ethanol detection by  $\text{In}_2\text{S}_3$  films matching a thickness around 2  $\mu\text{m}$ . As we will see in the following section, the optimal temperature can be shifted by the film thickness or the gas nature while remaining in the vicinity of  $350^\circ\text{C}$ . We think that this value allows a significant response comparison. **Fig. 5** illustrates dynamic responses during the alternating exposure to target gas and dry air. For each sensor, three response and recovery curves are shown.



**Fig. 5:** Dynamic response of  $\text{In}_2\text{S}_3$  films to 4000 ppm of Methanol, Ethanol and Acetone at  $350^\circ\text{C}$  for thickness varying from  $0.8 \mu\text{m}$  to  $6.1 \mu\text{m}$ .

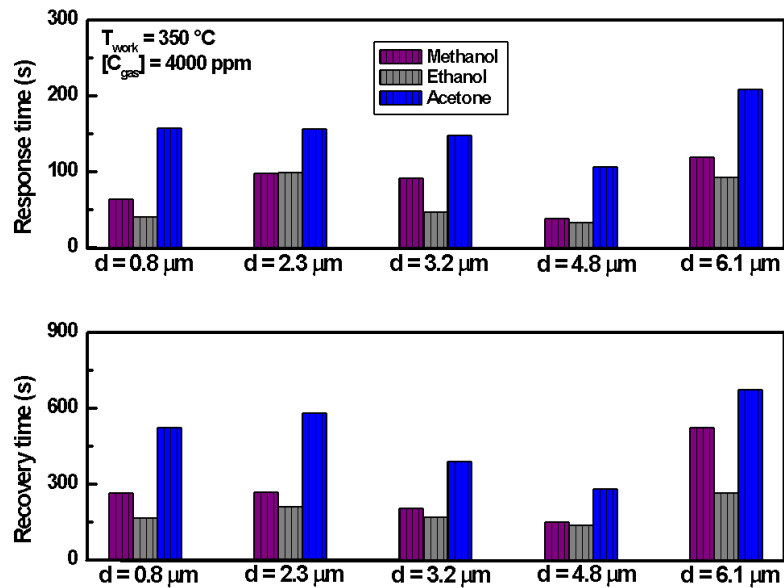
We note that for all the prepared sensors, during the exposure to target gas, the response increases quickly to an equilibrium value and then returns to the baseline when dry air is re-injected in the test chamber. This behavior is consistent with the sensing mechanism of n-type semiconductors. It is also observed that the response plot obtained is affected by the change of thickness. A possible explanation is that samples have different specific surface areas. In the case of smooth layers and low roughness ( $d = 0.8 \mu\text{m}$ ,  $d = 2.3 \mu\text{m}$ ,  $d = 3.2 \mu\text{m}$  / Root mean

squared roughness of 141 nm, 207 nm and 223 nm, respectively) the gas interaction is only taking place at the geometric surface. In the case of granular layer and high roughness ( $d = 4.8 \mu\text{m}$ ,  $R_q = 501 \text{ nm}$ ), the gas interaction can therefore take place at the surface of individual grains and at grain-grain boundaries [36]. So, such sensor presents a higher specific surface area involving abundant active adsorption sites which improve the gas response. This result confirms the proposal to improve the response by changing microstructure and morphology of sensors [37]. In the case of sample ( $d = 6.1 \mu\text{m}$ ,  $R_q = 1150 \text{ nm}$ ) cracks increase the electric potential barriers, reduce the current and diminish the sensing response. Indeed, the increase in resistance is related to the number of cracks in the semiconductor layer which depends on the applied deformation and the thickness of the film [38]. Despite the fact that the cracks can be the gas trapping path, it is also very possible that they cause an electrical rupture of these areas. We think that the active surface which describes the resistance decreases enormously with these cracks because they prevent the electrical contribution of a certain volume of material and therefore reduce the response of the sensor.

### 3.2.2 Rapidity

In a second stage, we investigated the time deposition effect on the sensing rapidity of  $\text{In}_2\text{S}_3$  thin films. The response time  $\tau_{\text{res}}$  is defined as the time required for the sensor to reach 90% of the sensor response, and the recovery time  $\tau_{\text{rec}}$  as that needed to reach 10% of the initial resistance baseline after the analyt gas has been purged. **Fig. 6** shows the comparison of samples with respect to their response time, tested by the vapors of Methanol, Ethanol and Acetone with 4000 ppm concentration and  $350^\circ\text{C}$  operating temperature. We note that the sensor prepared with thickness  $d = 4.8 \mu\text{m}$  presents the faster response. Also, the shortest response time corresponds to Ethanol gas for all samples (e.g.  $\tau_{\text{res}}(\text{ethanol}) = 33 \text{ s}$ ). In addition to this, **Fig. 6** illustrates the evaluation of recovery times which show a similar evolution- like

response time. We have checked that the sensor matching the thickness of 4.8  $\mu\text{m}$  has also the shortest recovery time (e.g.  $\tau_{\text{rec}}(\text{ethanol}) = 138$  s). Therefore, the performance of  $\text{In}_2\text{S}_3$  sensors evaluated by response and rapidity reveals that the sample matching the thickness of 4.8  $\mu\text{m}$  presents the best results.



**Fig. 6:** Response and recovery times of  $\text{In}_2\text{S}_3$  films to 4000 ppm of methanol, ethanol and acetone at 350 $^{\circ}\text{C}$ .

### 3.2.3 Reproducibility

Reproducibility was investigated by exposing  $\text{In}_2\text{S}_3$  sensors with different thicknesses to a variety of VOCs. Fig. 7 shows the dynamic response of sensors to various concentrations of Methanol, Ethanol and Acetone ranging from 2000 ppm to 10000 ppm, 1000 ppm to 5000 ppm and 4000 ppm to 20000 ppm respectively at the operating temperature of 350 $^{\circ}\text{C}$ . For each sensor, the sensor's response has an obvious increasing relationship with VOCs concentration, demonstrating that the sensor can offer more surface active sites and adsorb more VOCs molecules. Moreover, the sensor's response is affected by the layer's thickness



and the best response was performed with the thickness matching  $4.8\mu\text{m}$ . This fact reflects the reproducibility of the results detailed previously.

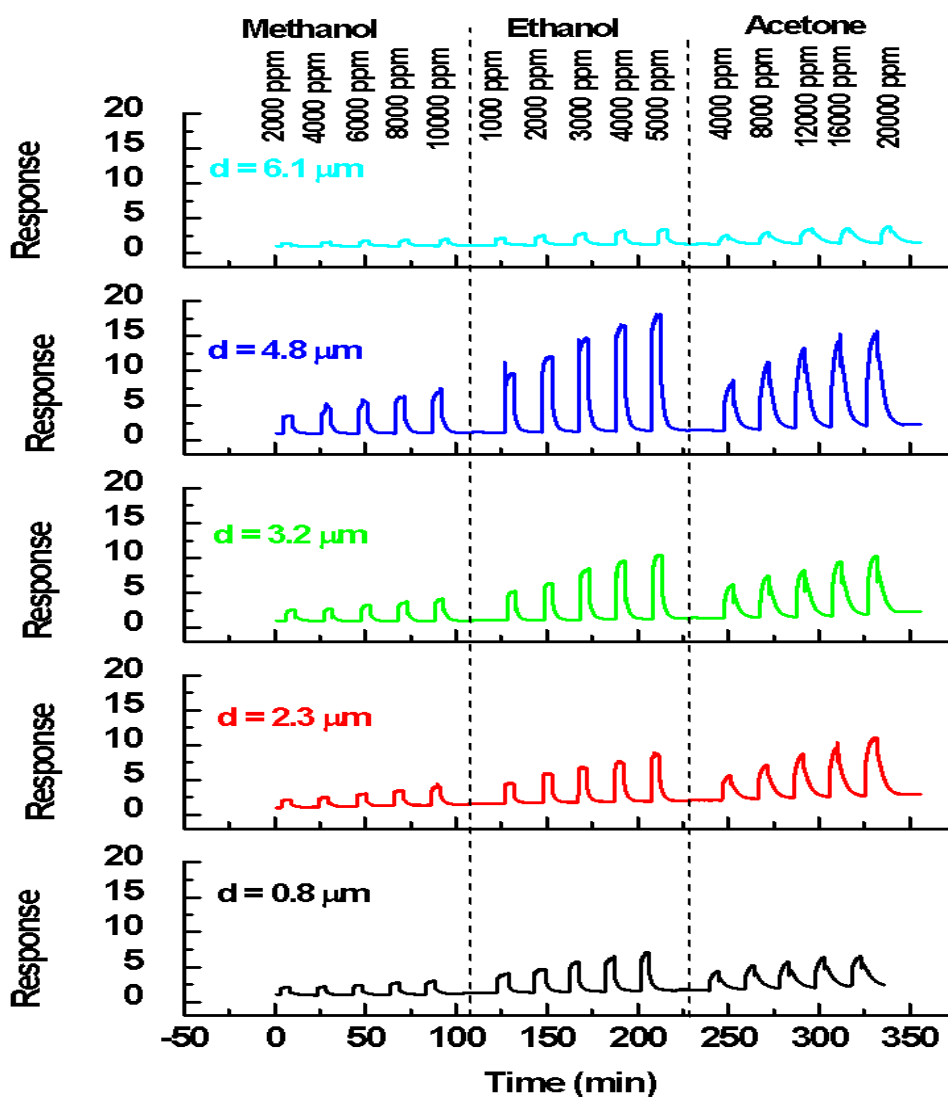


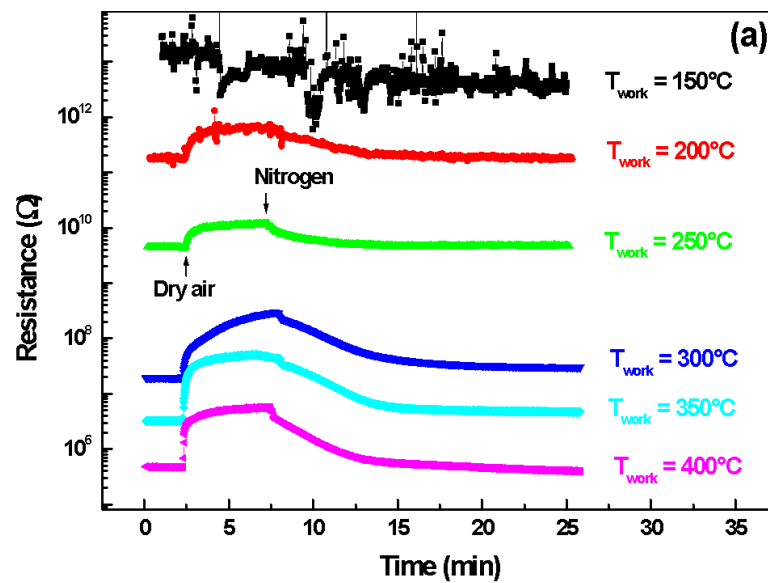
Fig. 7: Dynamic response of  $\text{In}_2\text{S}_3$  sensors with different thicknesses to various concentrations of methanol, ethanol and acetone at the operating temperature of  $350^\circ\text{C}$ .

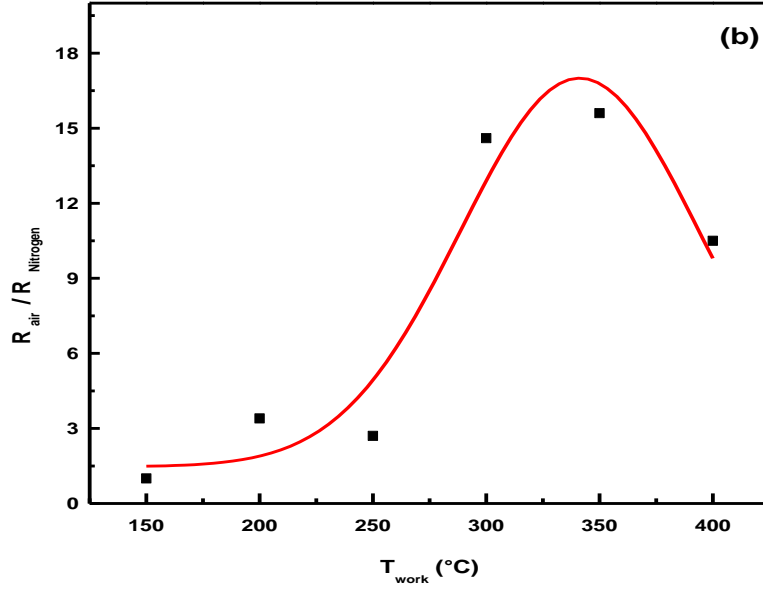
### 3.2.4 Gas sensing mechanism

In the following part, we propose to study the sensing mechanism and selectivity for some volatile organic compounds. We focused on the  $\text{In}_2\text{S}_3$  sample corresponding to the  $4.2 \mu\text{m}$  thickness.

### 3.2.4.1 Oxygen adsorption/desorption

Here, the adsorption and desorption of oxygen on a polycrystalline Indium Sulfide thin layers have been experimentally demonstrated by performing alternating exposure to Nitrogen and dry air at a working temperature ranging from  $150^\circ\text{C}$  to  $400^\circ\text{C}$ . **Fig. 8(a)** shows that resistance increases when dry air is introduced in the test chamber and decreases after its evacuation by Nitrogen for an operating temperature higher than  $200^\circ\text{C}$ .





**Fig. 8:** (a) Resistance change of  $\text{In}_2\text{S}_3$  film with time upon altering exposure to dry air and Nitrogen at operating temperature ranging from  $150^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ , (b) response of  $\text{In}_2\text{S}_3$  film to oxygen as a function of operating temperature.

In fact, under dry air an adsorption phenomenon occurs. Ho et al. [39] reported that because of Sulfur vacancies and Indium interstitials defects, the  $\beta\text{-In}_2\text{S}_3$  crystal can form easily surface oxidation states of  $\beta\text{-In}_2\text{S}_{3-3x}\text{O}_{3x}$  in ambient air (or  $\text{O}_2$ ) by chemical reaction of  $\text{In-O}$ . So, we think that the interaction of atmospheric oxygen with the surface of  $\text{In}_2\text{S}_3$  forms a layer of charged oxygen species, which traps electrons from the bulk of the material. The electrons trapped for this process are removed from the conduction band and are confined on the surface [36]. Consequently, a space charge layer is formed. The presence of negative surface charges leads to a band bending defined by potential barrier  $eV_s$  at the surface. This restricts the electron flow and decreases the conductivity. On the other hand, under Nitrogen, the resistance decreases reflecting the oxygen desorption phenomenon.

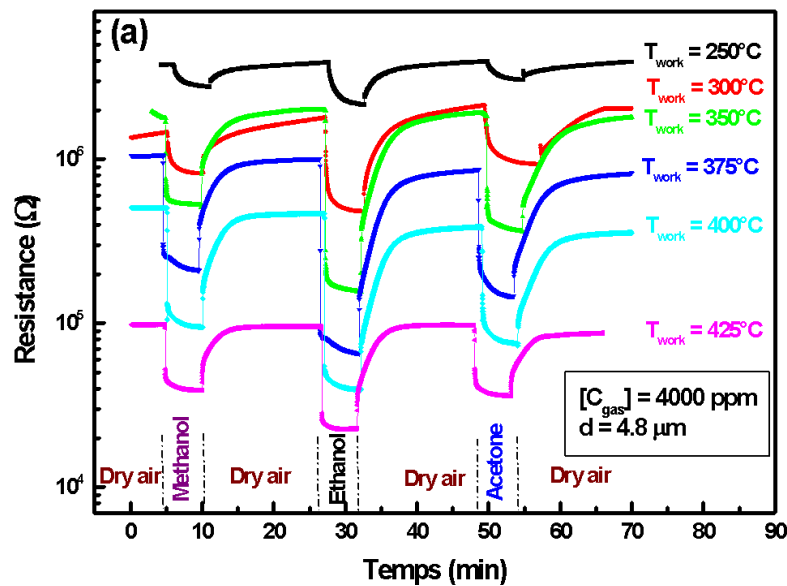
In this context, the study of the oxygen sensing response versus the operating temperature was illustrated in **Fig. 8(b)**. The response increases by increasing the working temperature up to 350°C and decreases above this temperature. This fact could be interpreted as a competition between the rates of oxygen adsorption and desorption, which is shown in the Lennard-Jones [40] equation:

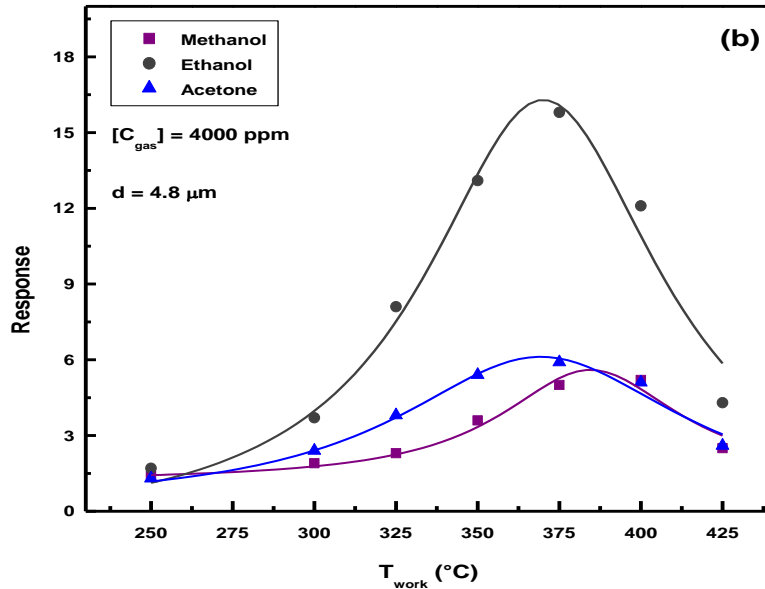
$$\frac{d\theta}{dt} = k_{ads} e^{-\frac{\Delta E_A}{kT}} - k_{des} e^{-\frac{(\Delta E_A + \Delta H)}{kT}} \quad (11)$$

where  $k_{ads}$  and  $k_{des}$  are respectively the rate constants for adsorption and desorption reactions,  $\Delta E_A$  the activate energy of chemisorption,  $\Delta H$  the heat of adsorption and  $\theta$  is the fraction of available surface sites covered.

### 3.2.4.2 Operating temperature effect

**Fig. 9(a)** demonstrates the resistance change during an alternating exposure to dry air and organic vapor (Methanol, Ethanol and Acetone) at 4000 ppm concentration. Measurements were made at different operating temperatures in the range of 250-425°C. The counting of these results is shown in **Fig. 9(b)**.





**Fig. 9:** (a) Resistance evolution of  $\text{In}_2\text{S}_3$  sensor upon exposure to 4000 ppm concentration of various organic vapors at operating temperatures in the range: 250°C-400°C, (b) sensing response of  $\text{In}_2\text{S}_3$  sensor vs. working temperature towards various organic vapors.

The evolution of the response versus the working temperature follows also Lennard-Jones equation and shows an optimal temperature for each gas. It clearly shows a direct correlation between oxygen adsorption and reducing gas detection. Indeed, responses to oxygen and reducing gases present a similar evolution and a neighboring optimal temperature.

The increase in operating temperature before the optimum value improves the oxygen adsorption and hence the VOCs response. On the other hand, desorption of all oxygen ionic species previously adsorbed occurs at high temperatures, which explains the response decrease to reducing gases beyond the optimum value.

We note that optimal temperature for Ethanol and Acetone is 365°C, whereas it is shifted to 385°C for Methanol gas. Similarly, such a trend has been studied by Bejaoui et al. [41]. They

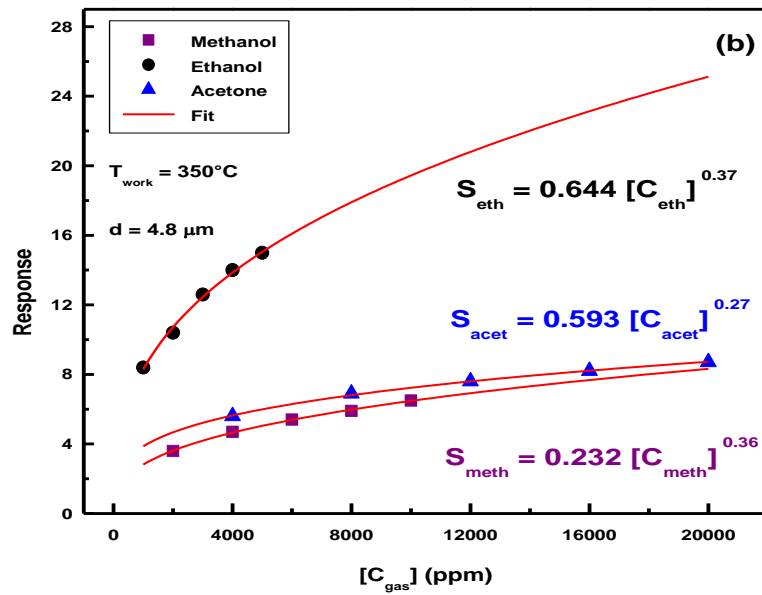
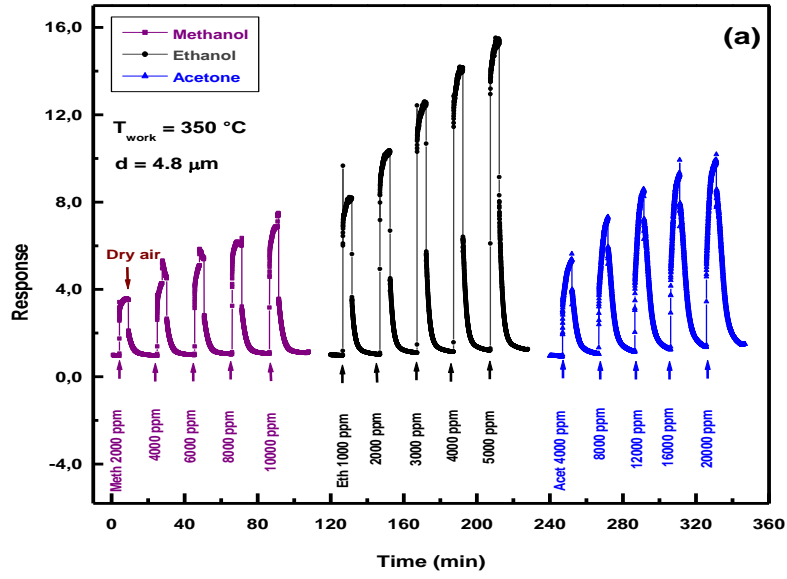
proposed a model simulating the interaction between sensors and reducing gases. They showed that the increase of the activation energy following a change of gas causes a shift of the optimal temperature towards a higher value. We also remarked that Ethanol response (16.2) is higher than the acetone one (6.3) at the same optimal temperature. This could be explained by the Ethanol and the Acetone molecules' size difference. Indeed, the surface cover rate is higher for the smaller molecules of Ethanol.

### 3.2.4.3 Gas concentration effect

In order to identify ionosorbed oxygen species, measurements were conducted on the  $\text{In}_2\text{S}_3$  sensor at a working temperature of  $350^\circ\text{C}$  by varying the concentration of Methanol, Ethanol and Acetone. The transient current during cycles (air/reducing gas/air) is shown in **Fig. 10(a)**. The fitting of the response versus gas concentration obtained in **Fig. 10(b)** shows a power law:

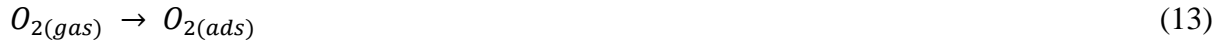
$$Response = Cte [C_{Reducing\ gas}]^\gamma \quad (12)$$

where  $\gamma \approx 1/3$  for the three analyzed gases. This typical value locates mainly  $O^{2-}$  ionosorbed oxygen on the material surface according to the metal oxide gas detection model proposed by Barsan and Weimer [36].

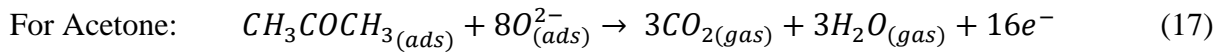
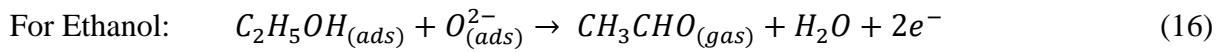
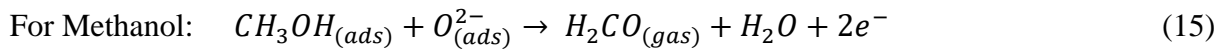


**Fig. 10:** (a) Dynamic response of  $\text{In}_2\text{S}_3$  sensor to various organics vapors concentrations at  $350^\circ\text{C}$ , (b) experimental and power fit of sensing response of  $\text{In}_2\text{S}_3$  sensor as a function of organic vapor concentration at  $350^\circ\text{C}$ .

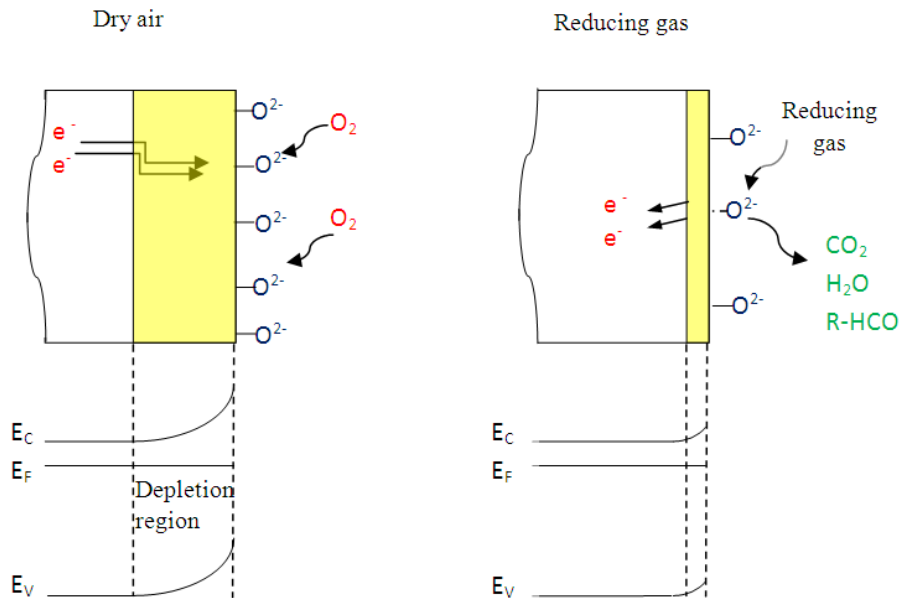
Thus, ionization equations of adsorbed oxygen can be written as follows:



In the same context, when the material is exposed to reducing gases, the organic molecules are oxidized by oxygen species  $O^{2-}$  and simultaneously the electrons are fed back into sensing body, the potential barrier is reduced and the conductivity increases. This mechanism can be expressed as follows:



So, oxygen plays the main element in reducing gas sensing response as detailed by the mechanism presented in **Fig.11**.

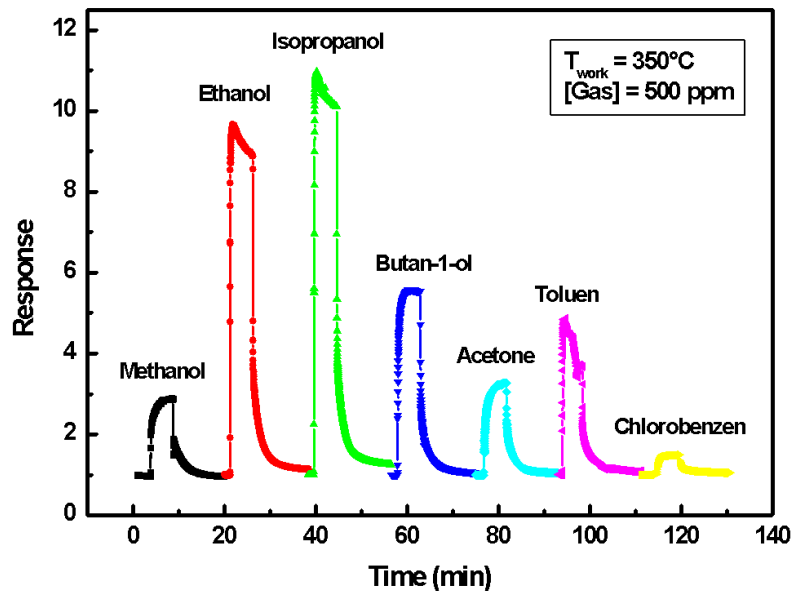


**Fig. 11:** Detection mechanism of organic vapor by  $In_2S_3$  sensor.



### 3.2.5 Selectivity

The efficiency of a sensor to respond to a certain gas in the presence of other gases is called selectivity. **Fig. 12** shows the dynamic response of an  $\text{In}_2\text{S}_3$  film ( $d = 4.8 \mu\text{m}$ ) to seven VOCs at a 500 ppm concentration and a working temperature of  $350^\circ\text{C}$ . This figure reveals that the relatively high responses are obtained with Isopropanol (10.5) and Ethanol (9.5). The middle response is observed with Butan-1-ol (5.8) and Toluene (4.5). Lastly, weak responses correspond to Methanol (2.9), Acetone (3.3) and Chlorobenzene (1.5) vapors. Therefore, we can't expect for the time being that our sensor can be selective. However, it is possible to analyze the different responses through a mathematical technique known as principal component analysis (PCA) [42]. This latter is a method of graphical data analysis which consists in finding the directions of space which best represents the correlations between the chosen variables of the measure [43]. This study is being planned for a future publication.



**Fig. 12:** Selectivity of  $\text{In}_2\text{S}_3$  sensor ( $d = 4.8 \mu\text{m}$ ).

A comparison of the developed sensor response to those of previously published Indium Oxide sensors is reported in **Table 3**. The results show that the Ethanol detection response of Indium sulfide  $\text{In}_2\text{S}_3$ -based sensor in the present work is not high but can be improved by enhancing gas adsorption or promoting specific chemical reactions via catalytic or electronic effects using bulk dopants and by the addition of metallic clusters or Oxide catalysts [44-46].

Material	Ethanol concentration (ppm)	Response	$\tau_{\text{rep}}/\tau_{\text{rec}}$ (s)	$T_{\text{opt}}$ ( $^{\circ}\text{C}$ )	Reference
$\text{In}_2\text{S}_3$	500	9.5	23/75	350	This work
$\text{In}_2\text{S}_3$	500	1.7	150/155	350	[30]
$\text{In}_2\text{O}_3$	50	5	40/38	300	[47]
3% Ag-doped $\text{In}_2\text{O}_3$	50	30	32/140	300	[47]
$\text{In}_2\text{O}_3/\text{Au}$ NRs	500	320	-/-	400	[48]
$\text{In}_2\text{O}_3$ Hierarchical architecture	100	1.5	-/-	260	[49]
$\text{In}_2\text{O}_3$ microcubes	500	55	-/-	210	[50]
Ce-doped $\text{In}_2\text{O}_3$	100	27.8	-/-	240	[51]
Pb-doped $\text{In}_2\text{O}_3$	100	32.5	2.2/0.7	250	[52]

**Table 3:** Sensing response of the developed indium sulfide sensor compared with previously published indium oxide sensors.

#### 4. Conclusion

$\text{In}_2\text{S}_3$  films were deposited on glass substrates by spray pyrolysis technique. Film thickness increases from 0.8  $\mu\text{m}$  to 6.1  $\mu\text{m}$  by increasing deposit time from 10 min to 90 min. XRD diffraction analysis reveals the formation of cubic  $\beta$ - $\text{In}_2\text{S}_3$  pure phase with (400) preferred orientation. The crystallite size varies in the narrow 39-52 nm range. The EDS measurements indicate that the S/In molar ratio remains constant for all the samples with an average value of 1.27. The morphological study by SEM shows that films were well covered, homogeneous and dense. The parameter  $R_q$  calculated from the roughness profile increases eventually with increasing thickness. Thus, the  $\text{In}_2\text{S}_3$  sample matching the thickness of 4.8  $\mu\text{m}$  combine high roughness and best crystallinity. Such results were correlated with its best sensing properties. We have fairly improved the  $\text{In}_2\text{S}_3$  sensor performances compared to that mentioned in the previous publication [30]. The response to 500 ppm Ethanol at 350°C is enhanced from 1.7 to 9.5. The response time and recovery time are improved from 150 s/155 s to 23 s/75 s respectively. The optimal working temperature is found to be around 385°C for Methanol and 365°C for both Ethanol and Acetone. Besides, oxygen adsorption versus working temperature were put forth and the sensing mechanism of the  $\text{In}_2\text{S}_3$  semiconductor was explained on the bases of the reaction between the reducing vapors with the chemisorbed oxygen ions  $\text{O}^{2-}$ . Nevertheless, these results revealing the potential of  $\beta$ - $\text{In}_2\text{S}_3$  in gas detection are encouraging for deepening the study in order to improve sensing properties and to test other gasses.

## Acknowledgments

This work was supported by Tunisian Ministry of Higher Education and Scientific Research, Spanish Ministry of Science and Innovation - FEDER Funds (MODENA Project CTQ2016-79461-R) and Fundación Ramón Areces (Spain, Project CIVP18A3940). NANOMAG group belongs to Galician Competitive Research Group ED431C-2017/22, programme co-funded by FEDER, and AEMAT Strategic Partnership (ED431E-2018/08,

Xunta de Galicia, Spain). The authors are grateful to Dr N. Ihzaz (High Institute of Applied Sciences and Technology, Gabes University, Tunisia) for useful discussions.

## References

- [1] B. Lawson, K. Aguir, T. Fiorido, V. Martini-Laithier, R. Bouchakour, S. Burtey, Ch. Reynard-Carette, M. Bendahan, Skin alcohol perspiration measurements using MOX sensors, *Sens. Actuators B. Chemical* 280 (2019) 306-312.
- [2] Q. Rong, Y. Zhang, T. Lv, K. Shen, B. Zi, Z. Zhu, J. Zhang, Q. Liu, Highly selective and sensitive methanol gas sensor based on molecular imprinted silver doped LaFeO<sub>3</sub> core-shell and cage Structures, *Nanotechnology* 29 (2018) 145503-145511.
- [3] Y. Xiong, Z. Zhu, D. Ding, W. Lu, Q. Xue, Multi-shelled ZnCo<sub>2</sub>O<sub>4</sub> yolk-shell spheres for high-performance acetone gas sensor. *Appl. Surf. Sci.* 443 (2018) 114-121.
- [4] X. Li, D. Lu, C. Shao, G. Lu, X. Li, Y. Liu, Hollow CuFe<sub>2</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> composite with ultrathin porous shell for acetone detection at ppb levels. *Sens. Actuators B* 258 (2018) 436-446.
- [5] O. Lupan, V. Postica, J. Gröttrup, A.K. Mishra, N.H. de Leeuw, J.F.C. Carreira, J. Rodrigues, N. Ben Sedrine, M.R. Correia, T. Monteiro, V. Cretu, I. Tiginyanu, D. Smazna,

Y.K. Mishra, R. Adelung, Hybridization of zinc oxide tetrapods for selective gas sensing applications. *ACS. Appl. Mater. Interfaces* 9 (4) (2017) 4084-4099.

[6] E. Wongrat, N. Chanlek, C. Chueaiarrom, W. Thupthimchun, B. Samransuksamer, S. Choopun, Acetone gas sensors based on ZnO nanostructures decorated with Pt and Nb. *Ceram. Int.* 43 (2017) 557-566.

[7] Ling Zhu, Yanqiong Li, Wen Zeng, Hydrothermal synthesis of hierarchical flower-like ZnO nanostructure and its enhanced ethanol gas-sensing properties, *Appl. Surf. Sci.* 427 (2018) 281-287.

[8] M. Asgari, F.H. Saboor, Y. Mortazavi, A.K. Khodadadi, SnO<sub>2</sub> decorated SiO<sub>2</sub> chemical sensors: Enhanced sensing performance toward ethanol and acetone. *Mater. Sci. Semicond. Process.* 68 (2018) 87-96.

[9] A. Gaiardo, B. Fabbri, V. Guidi, P. Bellutti, A. Giberti, S. Gherardi, L. Vanzetti, C. Malagù, G. Zonta, Metal Sulfides as Sensing Materials for Chemoresistive Gas Sensors, *Sensors* 16 (2016) 296-314.

[10] T. T. John, M. Mathew, C. S. Kartha, K. P. Vijayakumar, T. Abe, and Y. Kashiwaba, CuInS<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> thin film solar cell using spray pyrolysis technique having 9.5 % efficiency, *Solar Energy Materials and Solar Cells* 89 (2005) 27-36.

[11] M. Kraini, N. Bouguila, I. Halidou, A. Timoumi, S. Alaya, Properties of In<sub>2</sub>O<sub>3</sub> films obtained by thermal oxidation of sprayed In<sub>2</sub>S<sub>3</sub>, *Mater. Sci. Semicond. Process.* 16 (2013) 1388-1396.

[12] P.G.S. Abadi, M.S. Niasari, F. Davar, Hydrothermal synthesis, characterization and optical properties of 3D flower like indium sulfide nanostructures, *Superlattices and Microstructures* 53 (2013) 76-88.

[13] Z. Li, X. Tao, Z. Wu, P. Zhang, Z. Zhang, Preparation of In<sub>2</sub>S<sub>3</sub> nanoparticle by ultrasonic dispersion and its tribology property, *Ultrason Sonochemistry* 16 (2009) 221-225.

- [14] B. Asenjo, C. Sanz, C. Guillén, A.M. Chaparro, M.T. Gutiérrez, J. Herrero, Indium sulfide buffer layers deposited by dry and wet methods , *Thin Solid Films* 515 (2007) 6041-6044.
- [15] A. Timoumi, H. Bouzouita, M. Kanzari, B. Rezig, Fabrication and characterization of  $\text{In}_2\text{S}_3$  thin films deposited by thermal evaporation technique, *Thin Solid Films* 480 (2005) 124-128.
- [16] B. Tiss, M. Erouel, N. Bouguila, M. Kraini, K. Khirouni, Effect of silver doping on structural and optical properties of  $\text{In}_2\text{S}_3$  thin films fabricated by chemical pyrolysis, *J. Alloys Compd.* 771 (2019) 60-66.
- [17] N. Bouguila, M. Kraini, I. Halidou, E. Lacaze, H. Bouchriha, H. Bouzouita, Thickness effect on properties of sprayed  $\text{In}_2\text{S}_3$  films for Photovoltaic Applications, *J. Electron. Mater.* 45 (2016) 829-838.
- [18] N. Bouguila, M. Kraini, A. Timoumi, I. Halidou, C. Vázquez-Vázquez, M.A. López Quintela, S. Alaya, Substrate temperature effect on properties of sprayed  $\text{In}_2\text{S}_3$  films, *J. Mater. Sci: Mater. Electron* 26 (2015) 7639-7648.
- [19] T. Schulmeyer, A. Klein, R. Kneiese, M. Powalla, Band offset at the  $\text{CuGaSe}_2 / \text{In}_2\text{S}_3$  heterointerface, *Appl. Phys. Lett.* 85 (2004) 961-963.
- [20] R. Diehl, R. Nitsche, Vapour growth of three  $\text{In}_2\text{S}_3$  modifications by iodine transport, *J. Cryst. Growth* 28 (1975) 306.
- [21] J. Sterner, J. Malmstrom, L. Stolt, Study on ALD  $\text{In}_2\text{S}_3/\text{Cu}(\text{In,Ga})\text{Se}_2$  interface formation, *Prog. Photovoltaics* 13 (2005) 179.
- [22] S. Buecheler, D. Corica, D. Guettler, A. Chirila, R. Verma, U. Muller, T.P. Niesen, J. Palm, A.N. Tiwari, Ultrasonically sprayed indium sulfide buffer layers for  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$  thin-film solar cells, *Thin Solid Films* 517 (2009) 2312-2315.

- [23] E. Dalas, L. Kobotiatis, Primary solid-state batteries constructed from copper and indium sulphides, *J. Mater. Sci.* 28 (1993) 6595.
- [24] Yu-Jen Hsiao, Chung-Hsin Lu, Liang-Wen Ji, Teen-Hang Meen, Yan-Lung Chen, Hsiao-Ping Chi, Characterization of photovoltaics with  $\text{In}_2\text{S}_3$  nanoflakes/p-Si heterojunction, *Nanoscale Res. Lett.* 9 (2014) 32-38.
- [25] D.K. Nagesha, X. Liang, A.A. Mamedov, G. Gainer, M.A. Eastman, M. Giersig, J.J. Song, T. Ni, N.A. Kotov,  $\text{In}_2\text{S}_3$  Nanocolloids with Excitonic Emission:  $\text{In}_2\text{S}_3$  vs CdS Comparative Study of Optical and Structural Characteristics, *J. Phys. Chem. B* 105 (2001) 7490.
- [26] B. Hemanth Kumar, M.C. Santhosh Kumar, Indium sulfide based metal-semiconductor-metal ultraviolet-visible photodetector, *Sens. Actuators: A* 299 (2019) 111643.
- [27] Raid A. Ismail, Nadir F. Habubi, Mahmood M. Abbod, Preparation of high-sensitivity  $\text{In}_2\text{S}_3/\text{Si}$  heterojunction photodetector by chemical spray pyrolysis, *Opt. Quant. Electron* 48 (2016) 455-468.
- [28] S. Ghosh, M. Saha, V.D. Ashok, A. Chatterjee, S.K. De, Excitation dependent multicolor emission and photoconductivity of Mn, Cu doped  $\text{In}_2\text{S}_3$  monodisperse quantum dots, *Nanotechnology* 27 (2016) 155708-155724.
- [29] P. Cai, H. Song, Y. Lva, Hierarchical spheres  $\text{In}_2\text{S}_3$ -based cataluminescence sensor for ammonium sulfide, *Microchemical Journal* 138 (2018) 116-121.
- [30] R. Souissi, N. Bouguila, A. Labidi, Ethanol sensing properties of sprayed  $\text{In}_2\text{S}_3$  thin films, *Sens. Actuators B* 261 (2018) 522-530.
- [31] A. Labidi, E. Gillet, R. Delamare, M. Maaref, K. Aguir, Ethanol and ozone sensing characteristics of  $\text{WO}_3$  based sensors activated by Au and Pd, *Sens. Actuators B* 120 (2006) 338-345.

- [32] B.D. Cullity, Elements of X-ray Diffraction (Reading, MA: Addison-Wesley) 1978, Library of Congress Catalog Card No. 77-73950, ISBN 0-201-01174-3.
- [33] V. Bilgin, S. Kose, F. Atay, I. Akyuz, The effect of substrate temperature on the structural and some physical properties of ultrasonically sprayed CdS films, Mater. Chem. Phys. 94 (2005) 103-108.
- [34] N. Revathi, P. Prathap, K.T. Ramakrishna Reddy, Synthesis and physical behavior of In<sub>2</sub>S<sub>3</sub> films, Applied Surface Science 254 (2008) 5291-5298.
- [35] M. Krunks, O. Bijakina, T. Varema, V. Mikli, E. Mellikov, Structural and optical properties of sprayed CuInS<sub>2</sub> films, Thin Solid Films 338 (1999) 125-130.
- [36] N. Barsan, U. Weimar, Conduction model of metal oxide gas sensors, J. Electroceramic 7 (2001) 143-167.
- [37] A. Dey, Semiconductor metal oxide gas sensors: A review, Materials Science & Engineering B 229 (2018) 206-217.
- [38] D.R. Cairns, R. P. Witte, D.K. Sparacin, S.M. Sachsman, D.C. Paine, Gr.P. Crawford, R.R. Newton, Electric resistance dependent on the stress of indium oxide doped with tin on polymeric substrates, Applied Physics Letters 76 (11) (2000) 1425.
- [39] C. Ho, M. Lin, Y. Wang, Y. Huang, Synthesis of In<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>S<sub>3</sub> crystals for oxygen sensing and UV photo-detection, Sens. Actuators A 245 (2016) 119-126.
- [40] A. Labidi, C. Jacolin, M. Bendahan, A. Abdelghani, J. Guérin, K. Aguir, M. Maaref, Impedance spectroscopy on WO<sub>3</sub> gas sensor, Sens. Actuators B 106 (2005) 713-718.
- [41] A. Bejaoui, J. Guerin, K. Aguir, Modeling of a p-type resistive gas sensor in the presence of a reducing gas, Sens. Actuators B 181 (2013) 340-347.
- [42] X. Vanden Eynde, P. Bertrand, ToF-SIMS quantification of polystyrene spectra based on principal component analysis (PCA), Surface and Interface Analysis 25 (1997) 878-888.



- [43] M. Penza, G. Cassano, F. Tortorella, Gas recognition by activated  $\text{WO}_3$  thin film sensors array, *Sens. Actuators B* 81 (2001) 115-121.
- [44] L. Liu, P. Song, Z. Yang, Q. Wang, Ultra-fast responding  $\text{C}_2\text{H}_5\text{OH}$  sensors based on hierarchical assembly of  $\text{SnO}_2$  nanorods on cube-like  $\alpha\text{-Fe}_2\text{O}_3$ , *Journal of Materials Science: Materials in Electronics* 29, 7 (2018) 5446-5453.
- [45] P. Tyagi, A. Sharma, M. Tomar, V. Gupta, Metal oxide catalyst assisted  $\text{SnO}_2$  thin film based  $\text{SO}_2$  gas sensor, *Sens. Actuators B* 224 (2016) 282-289.
- [46] D. Hohl, The role of noble metals in the chemistry of solid-state gas sensors, *Sens. Actuators B* 1 (1990) 158-165.
- [47] K. Anand, J. Kaur, R.C. Singh, R. Thangaraj, Preparation and characterization of Ag-doped  $\text{In}_2\text{O}_3$  nanoparticles gas Sensor, *Chemical Physics Letters* 682 (2017) 140-146.
- [48] R. Xing, L. Xu, J. Song, C. Zhou, Q. Li, D. Liu, H.W. Song, Preparation and gas sensing properties of  $\text{In}_2\text{O}_3/\text{Au}$  nanorods for detection of volatile organic compounds in exhaled breath, *Sci. Rep.* 5 (2015)10717-10730.
- [49] S. Wang, J. Cao, W. Cui, L. Fan, X. Li, D. Li, Oxygen vacancies and grain boundaries potential barriers modulation facilitated formaldehyde gas sensing performances for  $\text{In}_2\text{O}_3$  hierarchical architectures, *Sens. Actuators B* 255 (2018) 159-165.
- [50] X. Zhou, F. Qu, B. Zhang, C. Jiang, M. Yang, Facile synthesis of  $\text{In}_2\text{O}_3$  microcubes with exposed {100} facets as gas sensing material for selective detection of ethanol vapor, *Materials Letters* 209 (2017) 618-621.
- [51] X. Liu, L. Jiang, X. Jiang, X. Tian, X. Sun, Y. Wang, W. He, P. Hou, X. Deng, X. Xu, Synthesis of Ce-doped  $\text{In}_2\text{O}_3$  nanostructure for gas sensor applications, *Applied Surface Science* 428 (2018) 478-484.

[52] A. Montazeri, F. Jamali-Sheini, Enhanced Ethanol Gas-Sensing Performance of Pb-Doped  $\text{In}_2\text{O}_3$  Nanostructures Prepared by Sonochemical Method, *Sens. Actuators B* 242 (2017) 778-791.