

## Accepted Manuscript

Title: Tin (IV) sulfide nanorods as a new gas sensing material

Author: A. Giberti A. Gaiardo B. Fabbri S. Gherardi V. Guidi  
C. Malagù P. Bellutti G. Zonta D. Casotti G. Cruciani



PII: S0925-4005(15)30473-1

DOI: <http://dx.doi.org/doi:10.1016/j.snb.2015.10.007>

Reference: SNB 19151

To appear in: *Sensors and Actuators B*

Received date: 30-7-2015

Revised date: 17-9-2015

Accepted date: 4-10-2015

Please cite this article as: A. Giberti, A. Gaiardo, B. Fabbri, S. Gherardi, V. Guidi, C. Malaggraveu, P. Bellutti, G. Zonta, D. Casotti, G. Cruciani, Tin (IV) sulfide nanorods as a new gas sensing material, *Sensors and Actuators B: Chemical* (2015), <http://dx.doi.org/10.1016/j.snb.2015.10.007>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Tin (IV) sulfide nanorods as a new gas sensing material

A. Giberti<sup>\*1,2</sup>, A. Gaiardo<sup>1,4</sup>, B. Fabbri<sup>1,3</sup>, S. Gherardi<sup>1</sup>, V. Guidi<sup>1,2,3</sup>, C. Malagù<sup>1,3</sup>, P. Bellutti<sup>4</sup>, G. Zonta<sup>1</sup>, D. Casotti<sup>1</sup>, G. Cruciani<sup>1</sup>

<sup>1</sup> Department of Physics and Earth Science, University of Ferrara, Via Saragat 1/c, 44122 Ferrara, Italy

<sup>2</sup> MIST E-R s.c.r.l., Via P. Gobetti 101, 40129 Bologna, Italy

<sup>3</sup> CNR-INO – Istituto Nazionale di Ottica, Largo Enrico Fermi 6, 50124 Firenze, Italy

<sup>4</sup> MNF - Micro Nano Facility, Bruno Kessler Foundation, Via Sommarive 18, 38123 Trento, Italy

## Abstract

Nanosized tin disulfide ( $\text{SnS}_2$ ) powder was synthesized through a simple and inexpensive process, then characterized via thermal, chemical, structural and morphological analyses. Conductometric gas sensors based on thick films of synthesized  $\text{SnS}_2$  were fabricated by means of screen-printing technology and their sensing properties tested vs. aldehydes, ketones and other gaseous compounds. We found that, at working temperature of 300 °C, the  $\text{SnS}_2$  films showed a strong selectivity vs the carbonyl group of aldehydes and ketones, proving that they can efficiently be detected even in complex mixtures with interferers. In comparison with its oxide counterpart,  $\text{SnS}_2$  proved to be more stable, in term of the long-term drift of the signal. On the base of the obtained results, practical applications of such a sensor have been addressed.

**Keywords:** gas sensor, tin sulfide, nanostructured  $\text{SnS}_2$  film

---

\* Corresponding author. Tel. +39 0532 974270

Email address: [giberti@fe.infn.it](mailto:giberti@fe.infn.it)

## Introduction

Tin (IV) sulfide is a mid-gap semiconductor ( $E_g = 2.35$  eV), which can be synthesized as different types of nanostructures, e.g., nanoparticles, nanotubes, nanobelts, nanoflakes etc. [1-3]. The physical and chemical properties of this IV-VI semiconductor are very interesting due to their possible application, as solar cell material [4], lithium batteries [5], field-effect transistors [6] and optoelectronics [7].

Even though the list of application fields is undoubtedly wide, so far the literature lacks of investigations on tin disulfide as a material for chemical sensing. For this particular application, up to now, conductometric gas sensors are mostly based on metal oxides. Such materials have been extensively investigated in the last decades, highlighting their great potential as gas sensors, but also showing some drawbacks, as their lack of stability, repeatability and selectivity [8,9] that are still currently limiting their use. For these reasons, it is crucial to investigate on new sensing materials that can possibly overcome the main disadvantages of metal oxides [10-12]. Among the above mentioned limitations for metal oxides, stability attracted the attention of scientific community due to its crucial role for fabricating reliable devices. Indeed, long-term stability problem could be related to a typical and characteristic defect of metal oxides: the oxygen vacancies [13,14]. The mobility of these defects is linked to the lack of thermodynamic equilibrium of oxygen with environment and it may be the reason of metal-oxides long-term instability. Therefore, the adoption of metal sulphide materials, where sulfur atoms take place of the oxygen one, can pave the way to an alternative, more reliable, sensing material for gas detection.

As far as tin disulfide is concerned, the relationship between the chemical adsorption of molecules and the electrical properties has seldom been investigated [15]. Such a relationship is responsible for the intimate connection between the electrical conductivity of a film and the chemical composition of the surrounding atmosphere and it is enhanced in the case of nanostructured semiconductors. Indeed, chemical adsorption of molecules accumulates charge in surface states, generating an electrostatic potential. In case of nanostructures, the depletion region of the surface potential is comparable with the size of the whole nanostructure; this results in a strong influence on the electrical properties of the material, thus opening their possible exploitation for gas sensing applications.

In order to investigate on the possible chemoresistive properties of this semiconductor, we synthesized nanosized SnS<sub>2</sub> powders and characterized them with XRD, TG/DTG/DTA, SEM and TEM techniques. Then, we studied the electrical resistance of films based on the as-synthesized powders upon exposure to a selection of different gaseous compounds, to investigate the sensitivity and selectivity of the SnS<sub>2</sub> sensors. The collected results are very interesting, since the samples showed an intense surface chemical activity which affects the resistivity of the material. In particular, they showed selectivity to molecules with ketone and aldehyde functional groups, proving the catalytic activity of SnS<sub>2</sub> surface vs. particular reactions and the possibility to employ SnS<sub>2</sub> as gas sensing material. Reproducibility and stability of the response was also tested for several weeks, with good results, whereas the response/recovery times were found in line with its oxide counterpart.

## Experimental details

### *Synthesis of SnS<sub>2</sub> powder and film deposition*

The sensing powder was synthesized starting from Sigma Aldrich reagents. The product was obtained as a precipitate in aqueous solution at standard temperature and pressure. First, 2.3 mmol of SnCl<sub>4</sub>·5H<sub>2</sub>O were dissolved in a beaker with 2 mL of HCl (37% m/v). Afterwards, 30 mL of distilled water were added to the resulted suspension and the obtained solution of Sn<sup>4+</sup> ions was stirred for 10 minutes. Then, 3.3 mmol of thioacetamide and 18 mL of water were added to this solution. The thioacetamide reacts with the water molecules leading to the formation of hydrogen sulfide [16,17], which is the source of S<sup>2-</sup> ions:



Then, the mixture was stirred again for 3 hours, forming a brown precipitate of  $\text{SnS}_2$ . The amount of available  $\text{S}^{2-}$  ions is controlled by pH, i.e. in an acid environment the  $\text{H}_2\text{S}$  dissociation is reduced and, as a consequence, the  $\text{S}^{2-}$  concentration. In this way, one can control the growth of the  $\text{SnS}_2$  crystallites. The precipitated product was isolated by vacuum filtration, washed with water and then with methanol. Finally, it was dried for 6 hours at  $40^\circ\text{C}$  in air.

The sensing paste was obtained by adding a proper amount of organic vehicles to the  $\text{SnS}_2$  powder and it was deposited on the alumina substrate by means of screen-printing technique. The resulting film thickness was about  $30\ \mu\text{m}$ . The substrates were equipped with both pre-deposited gold electrodes to provide the electrical contact for applying the voltage to the film and a heater on the back-side to set the desired working temperature. Then, the screen-printed films were subjected to thermal stabilization at  $180^\circ\text{C}$  in a muffle oven for 12 hours in air, to allow the evaporation of organic vehicles. The substrate was finally mounted on a suitable support to be interfaced with the electronic measuring system.

### Characterizations

Both the powder and the films were analyzed with Scanning Electron Microscopy and Energy Dispersive X-Ray spectroscopy (SEM-EDX spectroscopy) techniques, by means of a Zeiss EVO 40 microscope with an acceleration voltage of 30 kV, to investigate the morphology and chemical composition of the obtained material. TEM images were collected with a Hitachi H-800 model, equipped with a tungsten gun with maximum voltage of 200 kV.

The as-synthesized and heat treated  $\text{SnS}_2$  nanopowder were characterized by power X-Ray Diffraction (XRD) using a Bruker D8 Advance diffractometer with an X-ray tube operating at 40 kV and 40 mA, and equipped with a Si(Li) solid-state detector (SOL-X) set to measure  $\text{CuK}\alpha_{1,2}$  radiation. As-synthesized powders after thermal treatments were side-loaded on an aluminum holder, and zero-background holder respectively. Measuring conditions were from  $5$  through  $95^\circ 2\theta$  range,  $0.02^\circ 2\theta$  scan rate, counting time per step 4 and 6 s for as synthesized and thermally treated nanopowders, respectively. The phase identification was achieved by search-match using the EVA v.14.0 program by Bruker and the Powder Diffraction File database (PDF) v. 9.0.133. The crystallite size of the as synthesized nanopowder was determined by the Rietveld method, as implemented in TOPAS v.4.1 program by Bruker AXS [18]. The fundamental parameters approach was used for the line-profile fit [19-21]. The determination of crystallite size by TOPAS was accomplished by the Double-Voigt approach [22]. In particular, the crystallite size was calculated as volume-weighted mean column heights based on integral breadths of peaks.

Thermogravimetric (TG/DTG/DTA) curves of the screen-printing paste were recorded using a Netzsch 409 PC Luxx TG/DTA thermal analyzer. About 70 mg of samples were filled in a nickel crucible and analyzed in the range  $20$ - $600^\circ\text{C}$ , with heating rate of  $10^\circ\text{C min}^{-1}$  under air flow of  $20\ \text{ml h}^{-1}$ .

### 2.3 Gas measurements

The electrical conductance of the  $\text{SnS}_2$  sensors was measured in a test chamber by means of the flow-through technique. The sensors were kept at their working temperature under a flow of synthetic air for a few hours before the gas measurements, in order to allow the surface of the  $\text{SnS}_2$  grains to reach a thermodynamic

steady state. Air and gases were from certified bottles, and the injection in the chamber was carried out by means of a PC-driven mass-flow-controller. The conductance of the films was constantly recorded during the gas measurements through proper electronics interfaced to a data-acquiring system. The responses of the sensors were investigated at operating temperatures between 150 °C and 300 °C. Much higher temperatures must be avoided with this material, since it oxidizes to SnO<sub>2</sub> [23], whereas temperatures lower than 250 °C proved to be not sufficient to activate surface chemistry. The tested gases represent different categories of molecules, to test the surface reactivity of this semiconductor with respect to gas molecules with important chemical differences. Gas concentrations have been chosen taking into account the corresponding Threshold Limit Values (TLV). Tests were performed with CO (1 ppm, 10 ppm), benzene (5 ppm), methane (2500 ppm), H<sub>2</sub>S (1 ppm, 10 ppm), NO (10 ppm), acetaldehyde (1 ppm, 10 ppm) and acetone (1 ppm, 10 ppm). The same measurements were performed in dry air carrier and wet air carrier, by means of a bubbling system. In wet air carrier, the humidity level was around 20% relative humidity (RH). After we verified that humidity levels larger than RH ~ 20% had no significant effects on the response of the samples, we opted to perform the wet measurements with this relatively low level of humidity, to have more leeway in the dry component of the carrier.

### 3. Results and discussion

#### 3.1 Characterizations

The results of XRD measurements of the synthesized nanopowder are shown in Fig. 1 (red curve). From phase matching analysis it turned out that the material is monophasic and the peaks correspond to Berndtite-2T (space group P-3m1), confirming that the synthesis method yielded very high purity SnS<sub>2</sub>. Crystallite size from Rietveld profile fitting resulted ( $6.2 \pm 0.4$ ) nm.

The results of SEM-EDX measurements are shown in Fig. 2. It can be noticed the presence of clusters with dimensions up to about one micron. The EDX peaks and the result of the chemical analysis confirmed the purity of the obtained product, since no other chemical elements have been observed.

TEM analysis, (see in Fig. 3), evidences that the clusters observed in SEM images are composed by structures with nanorod-like morphology. The average dimensions of nanorods are about 20-30 nm in length and 5 nm thick. Such quite small dimensions are due to the acidic character of the synthesis environment, which allows a slow release of sulfur ions. The inset in Fig. 3 shows the SAED diffraction pattern, which confirms the crystal phase determination of XRD measurements. The interplanar distances were found to be 3.20, 2.74 and 1.79 Å, based on  $\lambda^2 = L^2/R^2$  formula, where  $\lambda$  is the wavelength of the electrons (0.037 nm at 100 kV),  $L$  is the camera length (40 cm) and  $R$  the radius of the diffraction rings.

Fig. 4 reports the TG/DTG/DTA analyses performed on the as-synthesized SnS<sub>2</sub> nanopowder. It can be observed an exothermic peak at about 120 °C, related to water loss until 135 °C. Another small weight loss starts from 135 °C until 300 °C, probably due to the evaporation of the last residuals of organic vehicles. At temperatures exceeding 450 °C, SnS<sub>2</sub> begins to transform into tin (II) oxide (SnO) and finally oxidizes to SnO<sub>2</sub>, which

corresponds to further weight loss [23]. Since the electrical characterizations showed better sensing performance at 300 °C as compared to lower temperatures, XRD analysis was carried out after six weeks of usage at 300 °C. The analysis, reported in Fig. 1 (blue curve on which only a negligible trace of cassiterite can be detected), showed the absence of any significant phase and chemical changes, thus proving the substantial stability of SnS<sub>2</sub> at this working temperature [24]. For this reason, we safely considered 300 °C as operating temperature for SnS<sub>2</sub>.

### 3.2 Gas sensing results

We firstly analyzed the films vs. the "3S-rule", i.e., sensitivity, selectivity and stability.

The sensitivity is defined as the slope of the response vs. the gas concentration. For an *n*-type semiconductor, the response to a reducing agent is calculated as:

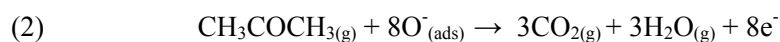
$$(2) \quad R = \frac{G_{\text{gas}} - G_{\text{air}}}{G_{\text{air}}}$$

where  $G_{\text{gas}}$  and  $G_{\text{air}}$  are the conductance values in gas and in air, respectively. To compare the resistivity of the samples with that of the typical SnO<sub>2</sub> nanostructures, the as-synthesized SnS<sub>2</sub> powder is about three times more resistive. We found the conductance values of the samples operating at 300 °C being in the range  $6-8 \times 10^{-8} \Omega^{-1}$ .

Results of the experiments for a SnS<sub>2</sub> sensor in dry condition are reported in Fig. 5. It can be noticed that at 250 °C the sensors were modestly responsive to the gases,  $R$  being in the range 0.05-0.5, and no particular selectivity was observed. Instead, at 300 °C, the responses were significantly improved. Indeed, at this operating temperature, the sensors strongly and selectively sensed the ketone and aldehyde functional groups, with an increase in response by almost two orders of magnitude. The responses to the other analytes under investigation were all negligible but hydrogen sulfide, for which a modest response (less than 8% with respect to acetone) was recorded.

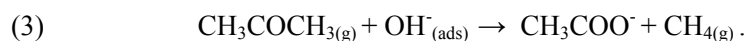
The performance of the sensing material was tested vs humidity. Fig. 6a and 6b show the dynamic responses of a SnS<sub>2</sub> thick-film sensor at 300 °C exposed to 10 ppm of acetone, 10 ppm of acetaldehyde and 10 ppm of H<sub>2</sub>S in dry and wet conditions, respectively. The temperature inside the test chamber was 28 °C. In Fig. 6c and 6d, the dynamic responses of the same sample in presence of 1 ppm gas concentration are also shown. From this measurements it is clearly observed that under wet conditions the response time is of the order of some minutes, whereas the recovery time is from 2 to 3 times longer, as under dry conditions, a feature similar to the behavior of traditional metal-oxide films [25-27]. Therefore, it is possible to conclude that humidity reduces the response by more than one order of magnitude. It is worth noting that the reduction factor was almost independent of the gas, therefore the presence of water vapor diminishes the sensitivity but does not alter the selectivity obtained in dry air. As a consequence of these measurements, it derives that the low detection limit for acetone falls in the sub-ppm range.

As in the case of metal-oxides, oxygen atoms are adsorbed on the surface of metal sulfides [28,29], and therefore they can be involved in the chemical reactions on the base of the transduction process [30]. Indeed, a possible chemical mechanism for the acetone detection by SnS<sub>2</sub> could be based on the oxidation of the molecule on the semiconductor's surface, involving an adsorbed oxygen ion and catalyzed by the semiconductor itself:



The function of the sulfur, in comparison to a metal, is to operate a different catalytic activity, resulting in different reaction steps and, as proved by the experiments, an improved selectivity.

In presence of water vapor, the reaction (1) enters into competition with the reaction of acetone with a weakly physisorbed hydroxyl group  $\text{OH}^-$  :



In this case, since there is no surface/gas charge transfer, the total conductance change is reduced, thus explaining the much weaker responses under humidity conditions. Given the high working temperature and the catalytic action of the sensitive material, the reaction may proceed to a further oxidation to acetate.

In order to investigate on the possible cross sensitivity between acetone and other gases, few interference tests were carried out. In particular, we choose acetaldehyde since among the tested gases it yielded a considerable response. In this experiment, performed in wet condition, we measured the response to a mixture of 1 ppm of both acetone and acetaldehyde. The result is reported in Fig. 7. As one can see, the presence of acetaldehyde hardly affects the response to acetone. This is a further proof of the very good selectivity of this sensing material to acetone, as well as of the importance of the non-linearity of the responses to different gases in conductometric gas sensors.

In order to verify the acetone response reproducibility over the time,  $\text{SnS}_2$  sensors were tested by exposing them to 10 ppm of acetone at different times, in a period lasting six weeks. The result is reported in Fig. 8 and they show quite interesting features of this material since both a modest response variation and the absence of a definite trend are the main characteristics.

It is remarkable to notice that the in-diffusion of oxygen in  $\text{SnO}_2$  annihilates oxygen vacancies, changing the doping level, whereas in  $\text{SnS}_2$  it replaces the sulfur atoms and annihilates sulfur vacancies, transforming the material in tin dioxide. Tin dioxide long-time drift may be associated to this phenomenon [13, 14], which could be a problem because in  $\text{SnO}_2$  the gas sensing achieves good performance at much higher working temperatures ( $> 400^\circ\text{C}$ ), where oxygen in-out diffusion is highly efficient. On the contrary,  $\text{SnS}_2$  shows very interesting performance at temperatures well below the critical temperature, probably circumventing in-out diffusion-related instabilities.

The observed  $\text{SnS}_2$  stability, both during single and the long-term data acquisitions, can open its use as sensing material. The observed remarkable selectivity to ketones and aldehydes envisages some interesting applications. This may be exploited in industrial environment and health-oriented applications. As an example, during the industrial production of plastic bottles, acetaldehyde is produced by thermal degradation of plastic polymers and an accurate control over the unintentional production of this chemical compound is important to avoid food contamination. As far as possible use of these sensors in health related field, it could be employed for the evaluation of acetone in human-breath, to diagnose pathologies which result in ketoacidosis, a metabolic state associated with unusually high concentrations of ketone bodies. Patients with untreated type 1 diabetes mellitus, prolonged alcoholism, pancreas and liver diseases can potentially develop ketoacidosis, running the risk of facing various disorders, such as kidney damage, cramps, dehydration, cardiac arrhythmia [31]. Therefore, a selective sensor for ketoacidosis-related compounds could be highly valuable in order to conceive a portable instrument capable of performing non-invasive measurements (consider for example the children or patients with severe mental diseases). For a possible use in this field, the experimental results previously reported obtained with 1 ppm of acetone in wet environment, closely simulate the conditions characterizing human breath

composition, where acetone concentration ranges 200 ppb - 2 ppm [31] is present in a water vapor. After we verified that humidity levels larger than RH ~ 20% had no significant effects on the conductance of the samples, we opted to perform the wet measurements with this relatively low level of humidity, to have more leeway in the dry component of the carrier.

After these findings, the potential of tin disulfide as gas sensing material becomes quite clear, especially considering acetone detection for health applications. Indeed, the major components of human breath, apart from nitrogen, oxygen and water vapor, are carbon dioxide, nitric oxide, acetone and volatile sulfur compounds, like hydrogen sulfide, methyl-mercaptan and dimethyl sulfide, also responsible for halitosis. Carbon dioxide does not represent a possible interferer because CO<sub>2</sub> shows very low reactivity with oxygen-covered semiconductor surfaces (a test was performed, confirming there is no interaction). Since the typical concentrations of these gases in human breath are 25-50 ppb for NO, 10-150 ppb for H<sub>2</sub>S [32-35], 200 ppb-2 ppm for acetone, it is evident that, comparing them to the tested concentrations, no interference to acetone detection can occur.

#### 4. Conclusions

Tin disulfide nanorods were synthesized and characterized from the chemical, structural, thermal and morphological perspective, resulting a high purity material with a single crystal phase and thermal stability up to 300°C. Conductometric gas sensors based on thick-films of SnS<sub>2</sub> were tested with several gases in dry and wet conditions, showing the best results at an operating temperature of 300°C. From the comparison with its counterpart oxide, tin disulfide showed a much higher resistivity, but a better selectivity with lower operating temperatures. The repeatability of the performances has been tested over six weeks with satisfying results. Tin disulfide proved to have very interesting gas sensing properties, since it showed a very good selectivity to acetone and acetaldehyde at concentrations ranging 1-10 ppm, in both dry and wet conditions. Simultaneous presence of acetone and acetaldehyde in wet conditions resulted in almost the same response of acetone only, proving that acetaldehyde cannot interfere with acetone detection. Possible applications were suggested, including plastic bottle industry and health-based applications with portable devices. Moreover, a possible mechanism of reaction has been proposed. It will be study deeply through suitable analysis to verify if the supposed chemical reaction really occurs.

#### References

- D. Ma, W. Zhang, Q. Tang, R. Zhang, W. Yu, Y. Qian, Large-scale hydrothermal synthesis of SnS<sub>2</sub> nanobelts, *J. Nanosci. Nanotechnol.* 5 (2005) 806-809.
- H. Chang, E. In, K.-J. Kong, J.-O. Lee, Y. Choi, B.-H. Ryu, First-principles studies of SnS<sub>2</sub> nanotubes: A potential semiconductor nanowire, *J. Phys. Chem. B* 109 (2005) 30-32.
- H. Sun, M. Ahmad, J. Luo, Y. Shi, W. Shen, J. Zhu, SnS<sub>2</sub> nanoflakes decorated multiwalled carbon nanotubes as high performance anode materials for lithium-ion batteries, *Mater. Res. Bull.* 49 (2014) 319-324.



- B. Yang, X. Zuo, H. Xiao, SnS<sub>2</sub> as low-cost counter-electrode materials for dye-sensitized solar cells, *Mater. Lett.* 133 (2014) 197-199.
- W. Deng, X. Chen, Z. Liu, A. Hu, Q. Tang, Z. Li, Y. Xiong, Three-dimensional structure-based tin disulfide/vertically aligned carbon nanotube arrays composites as high-performance anode materials for lithium ion batteries, *J. Power Sources* 277 (2015) 131-138.
- L. Wang, L. Gao, H. Song, High-performance top-gated monolayer SnS<sub>2</sub> field-effect transistors, *Advanced Optoelectronics for Energy and Environment, AOEE 2013, Wuhan (China) 25-26 May 2013*.
- X. Liu, H. Bai, Hydrothermal synthesis of visible light active zinc-doped tin disulphide photocatalyst for the reduction of aqueous Cr(VI), *Powder Technol.* 237 (2013) 610-615.
- D.R. Miller, S.A. Akbar, P.A. Morris, Nanoscale metal oxide-based heterojunctions for gas sensing: A review, *Sens. Actuators B* 204 (2014) 250-272.
- M.C. Carotta, A. Cervi, A. Giberti, V. Guidi, C. Malagù, G. Martinelli, D. Puzzovio, Ethanol interference in light alkane sensing by metal-oxides, *Sens. Actuators B* 136 (2009) 405-409.
- N.A. Travlou, M. Seredych, E. Rodriguez-Castellon, T.J. Bandoz, Activated carbon-based gas sensors: Effects of surface features on the sensing mechanism, *J. Mater. Chem.* 3 (2015) 3821-3831.
- A. Giberti, D. Casotti, G. Cruciani, B. Fabbri, A. Gaiardo, V. Guidi, C. Malagù, G. Zonta, S. Gherardi, Electrical conductivity of CdS films for gas sensing: Selectivity properties to alcoholic chains, *Sens. Actuators B* 207 (2015) 504-510.
- A. Giberti, B. Fabbri, A. Gaiardo, V. Guidi, C. Malagù, Resonant photoactivation of cadmium sulfide and its effect on the surface chemical activity, *Appl. Phys. Lett.* 104 (2014) 222102.
- C. Malagù, A. Giberti, S. Morandi, C.M. Aldao, Electrical and spectroscopic analysis in nanostructured SnO<sub>2</sub>: "long-term" resistance drift is due to in-diffusion, *J. Appl. Phys.* 110 (2011) 093711.
- C.M. Aldao, D.A. Mirabella, M.A. Ponce, A. Giberti, C. Malagù, Role of intragrain oxygen diffusion in polycrystalline tin oxide conductivity, *J. Appl. Phys.* 109 (2011) 063723.
- W. Shi, L. Huo, H. Wang, H. Zhang, J. Yang, P. Wei, Hydrothermal growth and gas sensing property of flower-shaped SnS<sub>2</sub> nanostructures, *Nanotechnology* 17 (2006) 2918-2924.
- A. Dumbrava, C. Badea, G. Prodan, I. Popovici, V. Ciupina, Zinc sulfide fine particles obtained at low temperature, *Chalcogenide Letters* 6 (2009) 437-443.
- Y. C. Zhang, Z. N. Du, K. W. Li, M. Zhang, Size-controlled hydrothermal synthesis of SnS<sub>2</sub> nanoparticles with high performance in visible light-driven photocatalytic degradation of aqueous methyl orange, *Separation and Purification Technology* 81 (2011) 101-107.
- Bruker AXS: TOPAS V4: General profile and structure analysis software for powder diffraction data. - User's Manual, Bruker AXS, Karlsruhe, Germany, 2008.
- R.W. Cheary, A.A. Coelho, A fundamental parameters approach to X-ray line-profile fitting, *J. Appl. Crystallogr.* 25 (1992) 109-121.

- R. W. Cheary, A.A. Coelho, J.P. Cline, Fundamental Parameters LineProfile Fitting in Laboratory Diffractometers, *J. Res. Natl. Inst. Stand. Technol.* 109 (2004) 1-25.
- A. Kern, A.A. Coelho, R.W. Cheary, Convolution based profile fitting. *Diffraction Analysis of the Microstructure of Materials*, edited by Mittemeijer, E.J. & Scardi, P. Materials Science, Springer, Germany, 2004.
- D. Balzar, Voigt-function model in diffraction line-broadening analysis. - *Microstructure Analysis from Diffraction*, edited by R. L. Snyder, H. J. Bunge, and J. Fiala, International Union of Crystallography, 1999.
- M. Yang, Y.C. Zhang, W.M. Dai, K. Hang, Y.Q. Pan, Synthesis of SnS<sub>2</sub>/SnO<sub>2</sub> nanocomposite for visible light-driven photocatalytic reduction of aqueous Cr(VI), *Key Eng. Mat.* 538 (2013) 46-49.
- J. Madarász, P. Bombicz, M. Okuyaa, S. Kanekoa, Thermal decomposition of thiourea complexes of Cu(I), Zn(II), and Sn(II) chlorides as precursors for the spray pyrolysis deposition of sulfide thin films, *Solid State Ionics* 141–142 (2001) 439–446.
- D. Haridas, V. Gupta, Enhanced response characteristics of SnO<sub>2</sub> thin film based sensors loaded with Pd clusters for methane detection, *Sens. Actuators B* 166 (2012) 156-164. doi:10.1016/j.snb.2012.02.026
- A. Giberti, M.C. Carotta, B. Fabbri, S. Gherardi, V. Guidi, C. Malagù, High-sensitivity detection of acetaldehyde, *Sens. Actuators B* 174 (2012) 402-405.
- V. Guidi, M.C. Carotta, B. Fabbri, S. Gherardi, A. Giberti, C. Malagù, Array of sensors for detection of gaseous malodors in organic decomposition products, *Sens. Actuators B* 174 (2012) 349-354.
- R. R. Chianelli, G. Berhault, B. Torres, Unsupported transition metal sulfide catalysts: 100 years of science and application, *Catalysis Today* 147 (2009) 275-286.
- S. J. Tauster, T. A. Pecoraro, R. R. Chianelli, Structure and properties of molybdenum sulfide: correlation of O<sub>2</sub> chemisorption with hydride sulfurization activity, *Journal of Catalysis* 63 (1980) 515-519.
- L.P. Chikhale, J.Y. Patil, A.V. Rajgure, F.I. Shaikh, I.S. Mulla, S.S. Suryavanshi, Structural, morphological and gas sensing properties of undoped and Lanthanum doped nanocrystalline SnO<sub>2</sub>, *Ceramics International* 40 (2014) 2179–2186.
- P.S. Hamblin, D.J. Topliss, N. Chosich, D.W. Lording, J.R. Stockigt, Deaths associated with diabetic ketoacidosis and hyperosmolar coma, *Med. J. Aust.* 151 (1989) 439-441.
- C. Di Natale, R. Paolesse, E. Martinelli, R. Capuano, Solid state gas sensors for breath analysis: A review, *Analytica Chimica Acta* 824 (2014) 1-17 doi:10.1016/j.aca.2014.03.014
- J. Zhang, X. Wang, Y. Chen, W. Yao, Exhaled hydrogen sulfide predicts airway inflammation phenotype in COPD, *Respir Care*. 60 (2015) 251-258. doi: 10.4187/respcare.03519
- D. Smith, P. Spanel, SIFT-MS and FA-MS methods for ambient gas phase analysis: developments and applications in the UK, *Royal Society of Chemistry* (2014), DOI: 10.1039/c4an02049a

C.F. Toombs, M.A. Insko, E.A. Wintner, T.L. Deckwerth, H. Usansky, K. Jamil, B. Goldstein, M. Cooreman, C. Szabo, Detection of exhaled hydrogen sulphide gas in healthy volunteers during intravenous administration of sodium sulphide, *Br. J. Pharmacol.* 69 (2010) 626-636.

Alessio Giberti

Bachelor in Theoretical Physics at the University of Ferrara in 2000, he obtained PhD in Physics of Matter in 2004 at the Physics Department of the University of Ferrara. His research since PhD is focused on the field of semiconductor gas sensors based on nanostructured metal oxides, with particular interest toward the electrical and selectivity properties.

Cesare Malagù

Bachelor in Physics at the University of Ferrara in 1997, he got his PhD in 2001 in experimental physics. Postdoc with the National Institute of Physics of Matter he received a four year research grant starting from 2001. Fellow at the University of Wales, Swansea in 2002. Research activity, carried out at the Sensors and Semiconductors laboratory of the University of Ferrara, is mainly based on the modeling of transport phenomena in nanostructured semiconductors.

Vincenzo Guidi

Bachelor in Physics at the University of Ferrara in 1990, fellow at "Budker Institute for Nuclear Physics" of Novosibirsk (Russia) in 1991. Thesis of doctorate in experimental physics at Legnaro National Laboratories in 1994. Researcher in experimental physics at University of Ferrara. Research activity, carried out at the Sensors and Semiconductors laboratory of the University of Ferrara, has consisted of investigations on basic phenomena in semiconductors and to practical implementations of sensing devices. Author of more than 140 articles in peer-reviewed journals and of more than 100 contributions to the proceedings of international conferences, reviewer and/or editors of numerous journals of Physics and Electronics, organizer of several national and international conferences and editor of the proceedings.

Barbara Fabbri

She obtained her master degree in Physics at University of Ferrara in 2011. Currently she is a PhD student involved in the field of gas sensors and micromachining.

Andrea Gaiardo

He obtained his Degree in Chemistry at the University of Ferrara in 2011 and the Master's Degree in Chemical Sciences at the University of Ferrara in 2013. Now, his work is focused in the field of innovative inorganic semiconductors for applications in gas sensing. He started his PhD in Physics at the University of Ferrara in November 2014.

Davide Casotti

Bachelor in Geology at the University of Ferrara in 2010. He received research grants from 2010 to 2013 to work on TiO<sub>2</sub> nanopowders, silica mesopores and hybrid organic-inorganic materials. In 2014 he started his PhD in Nanosciences and Nanotechnologies at University of Modena e Reggio Emilia.

Sandro Gherardi

Bachelor in Physics Technologies at the University of Ferrara in 2002. Research activity carried out at the Sensors and Semiconductors laboratory of the University of Ferrara about gas sensing and industrial applications of monitoring devices by nanostructured semiconductor based sensors.

Giuseppe Cruciani

Full Professor of Mineralogy at the University of Ferrara. Graduate with honor in Geological Sciences in 1993 at the University of Perugia, there he got a PhD in Mineralogy (Crystallography) and Petrology in 1989. Visiting scientist in 1995 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Member 2008-2010 of the chemistry review committee for project selection at ESRF, still in the proposal review panel for hard condensed matter-structures at the Elettra synchrotron in Trieste, Italy. Past President 2012-2013 of the Italian Society of Mineralogy and Petrology, is Associate Editor of the European Journal of Mineralogy. Major research fields in crystallography and crystal-chemistry of zeolite-like minerals and their synthetic analogues, and of many other silicate and oxide systems. Experimental skills mostly focused on single crystal and powder diffraction, both with conventional X-rays and large scale facility radiation (synchrotron X-rays and neutrons)

Giulia Zonta

She received the Bachelor's Degree in Physics and Astrophysics in December 2010 (110/110 cum laude) and the Master's Degree in Physics in October 2013 (110/110), at the University of Ferrara. In January 2014 she started her Ph.D. in Matter Physics, working with the Sensors Team, coordinated by Dr. Cesare Malagù. In the April of the same year she obtained the recognition "Ferrara School of Physics", that rewards the internationality of her Master's thesis work. Currently her research focuses on the study of the physic-chemical behavior of chemoresistive nanostructured gas sensors, put in contact with volatile organic compounds (VOCs) of medical interest. With her team she won Unife Cup 2013, a business plan competition that rewards innovative start-ups and Start Cup Emilia Romagna 2014, with the objective to create a start-up for the realization of devices for

medical screenings. Now she is the co-supervisor of two students which are working for the Bachelor's and Master's Degree in Physics respectively.

Pierluigi Bellutti

He received his Physical-Chemistry Laurea degree in 1984 and then started his research activity in silicon microtechnology, mainly on CCD and CMOS technologies. From 2000 till 2013 has been managing the MicroTechnologies Lab at FBK, in which R&D and production of new types of silicon radiation sensors and MEMS are carried out. Since January 2014 he is managing the MNFacility, where the Microtechnologies activities have been joined with those of Material Characterization.

## Figure captions

Fig. 1: Red curve: XRD pattern of the as-synthesized  $\text{SnS}_2$  powder. The expected lines for  $\text{SnS}_2$  (space group P-3m1) as in PDF card no. 23-0677 are marked in red while the blue marks are those expected for Cassiterite,  $\text{SnO}_2$  (PDF card no. 41-1445). Blue curve: XRD pattern of the same powder after six weeks operating at 300 °C.

Fig. 2: SEM image with EDX analysis of the synthesized powder.

Fig. 3: TEM image with 200k magnification. The inset shows the SAED diffraction pattern.

Fig. 4: TG/DTG/DTA curves measured on as-synthesized  $\text{SnS}_2$  powder.

Fig. 5: Summary of the obtained responses in dry condition, at 250 °C and 300 °C.

Fig. 6: Dynamic responses of a  $\text{SnS}_2$  film at 300 °C to 10 ppm and 1 ppm of acetone, acetaldehyde and  $\text{H}_2\text{S}$  in dry and wet condition. The temperature inside the test chamber was 28°C.

Fig. 7: Cross sensitivity of acetone (1 ppm) with acetaldehyde (1 ppm).

Fig. 8: Repeatability of the response to 10 ppm of acetone.

Figure 1

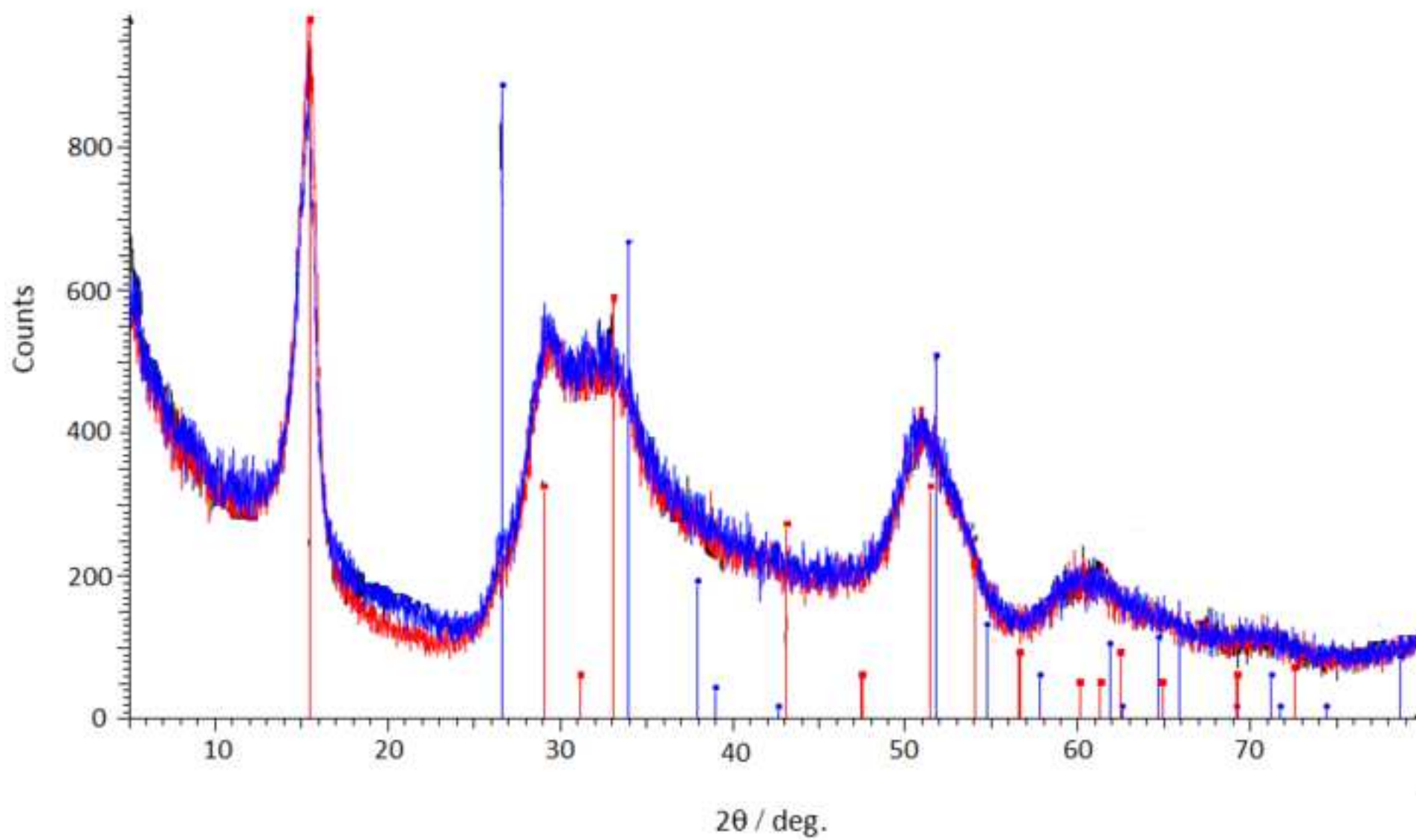


Figure 2

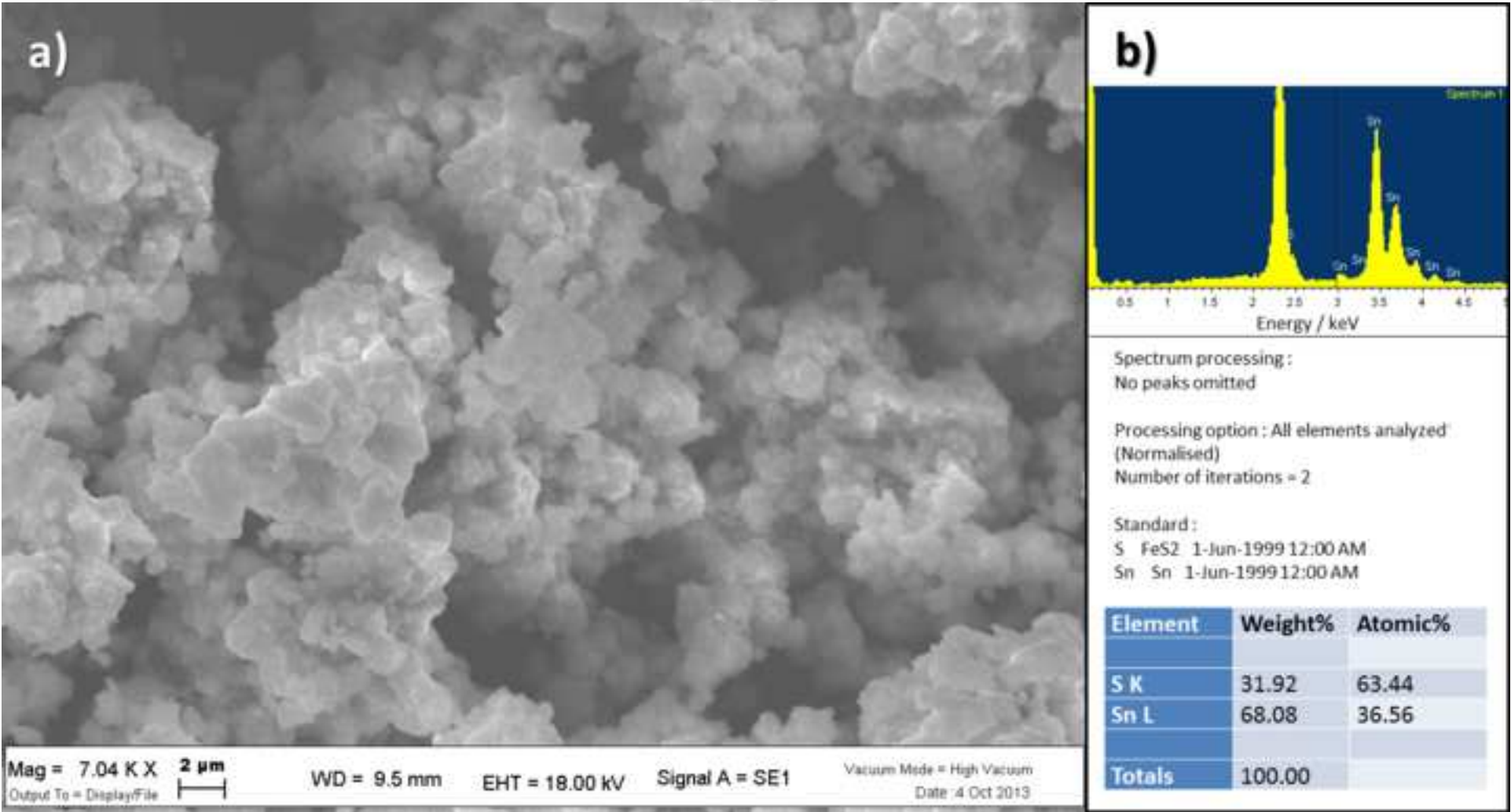


Figure 3

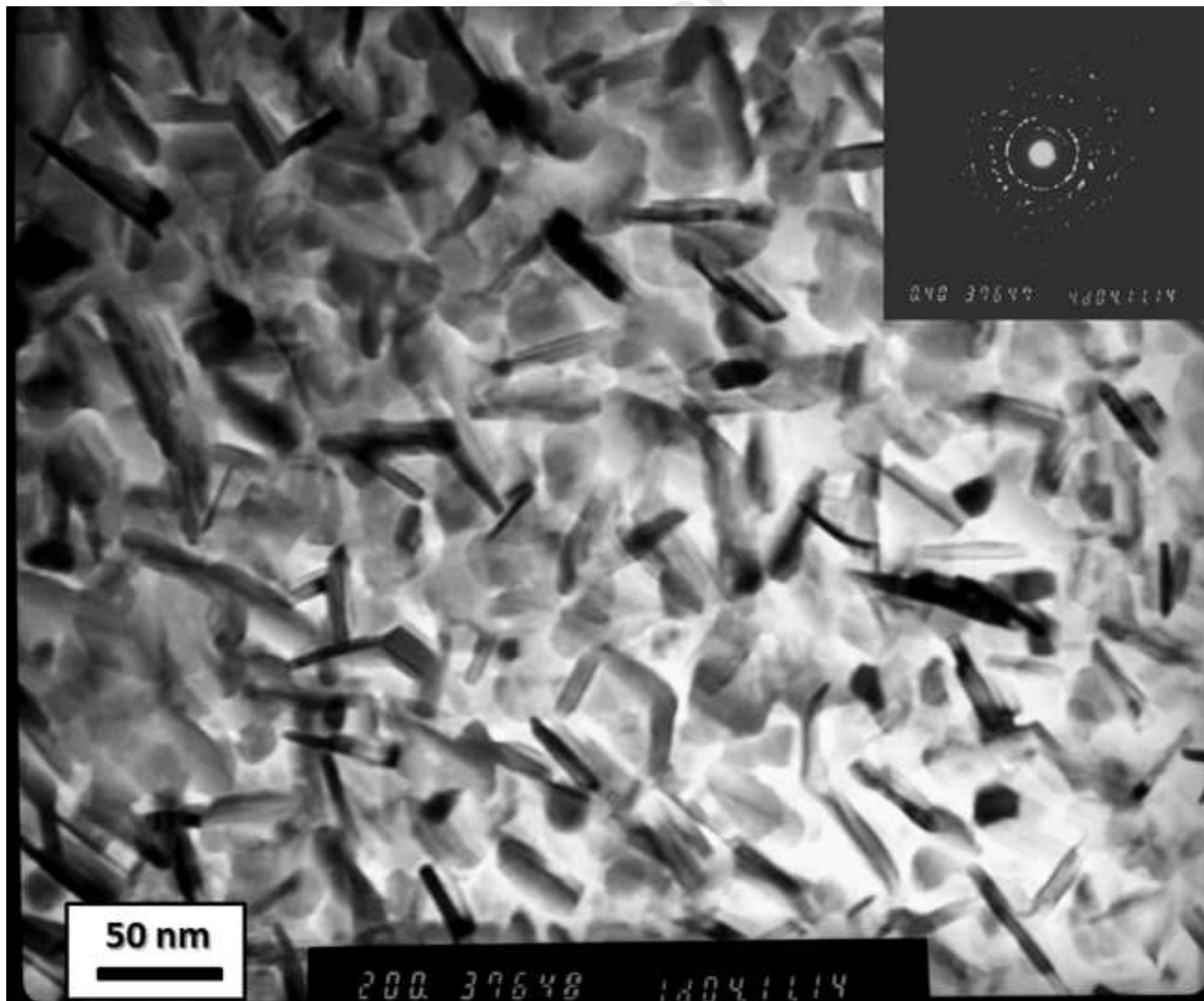




Figure 4

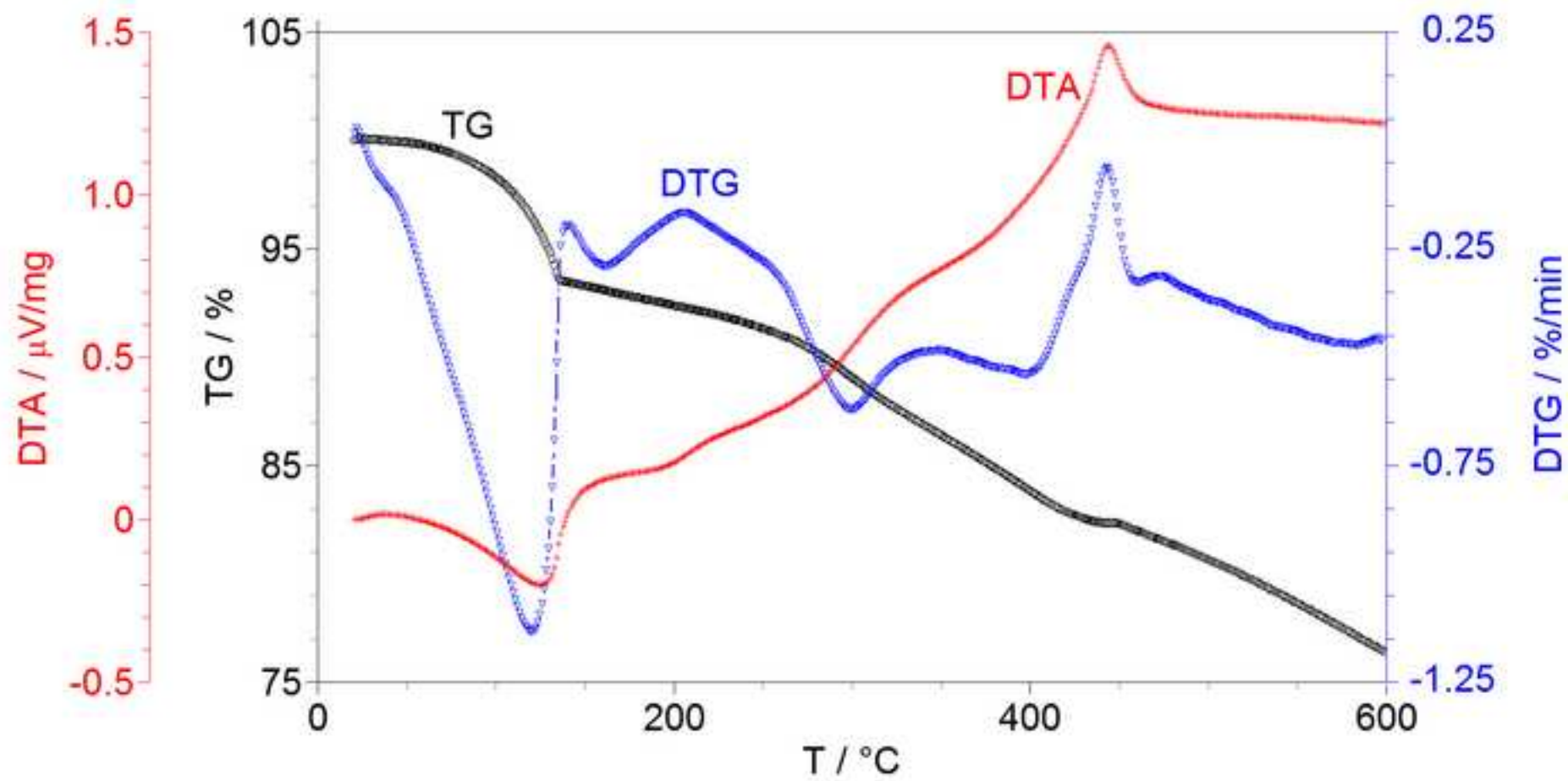


Figure 5

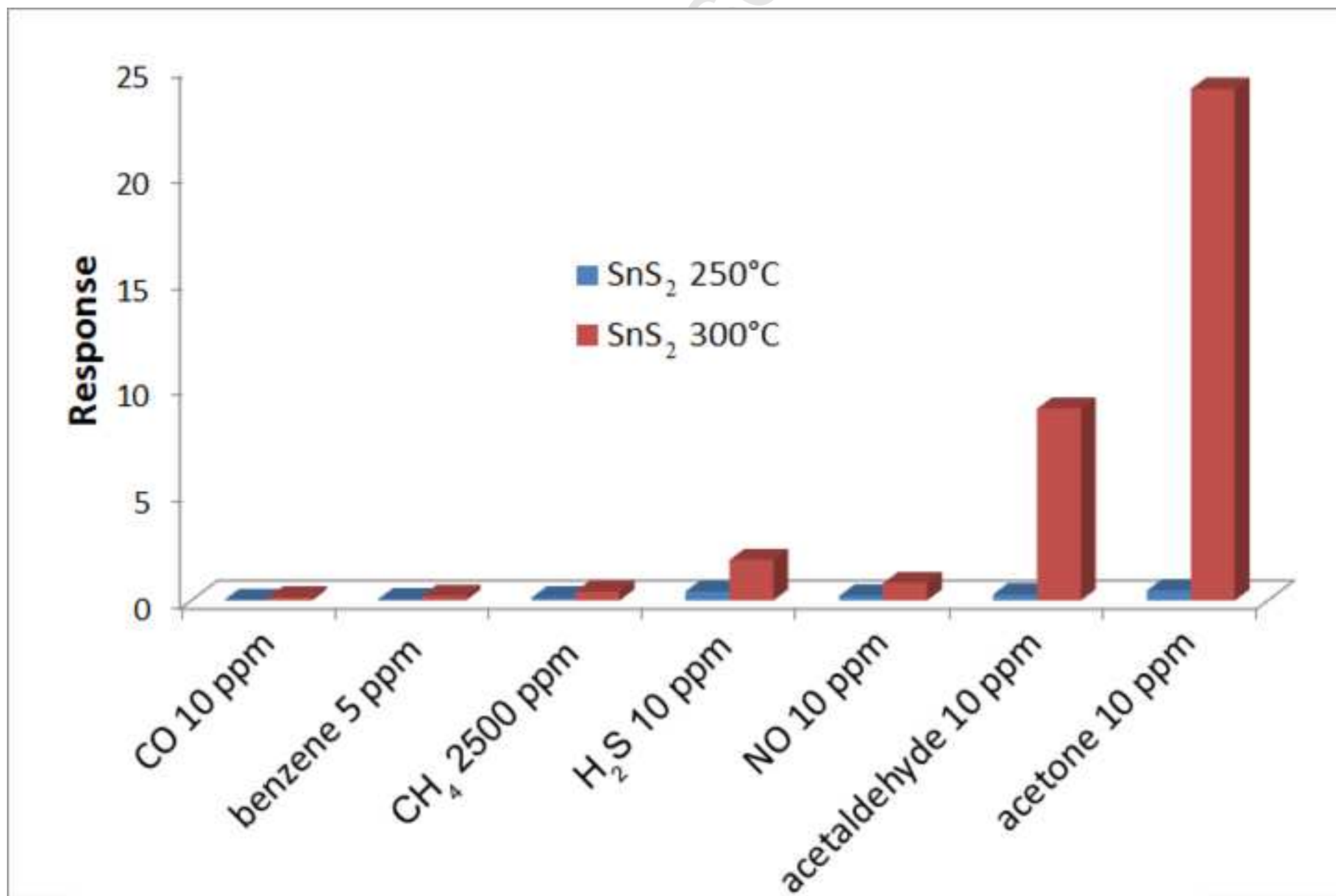


Figure 6

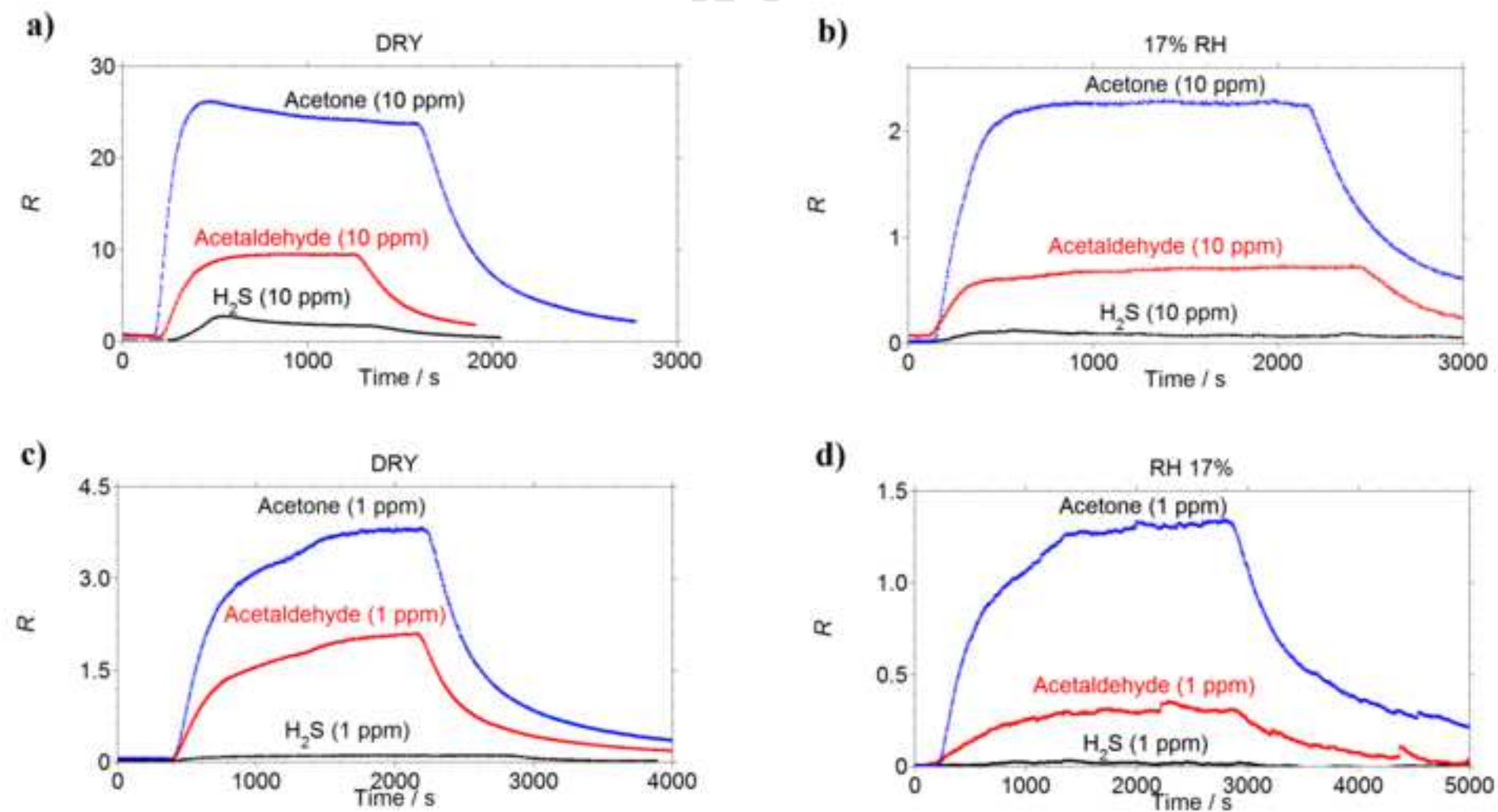


Figure 7

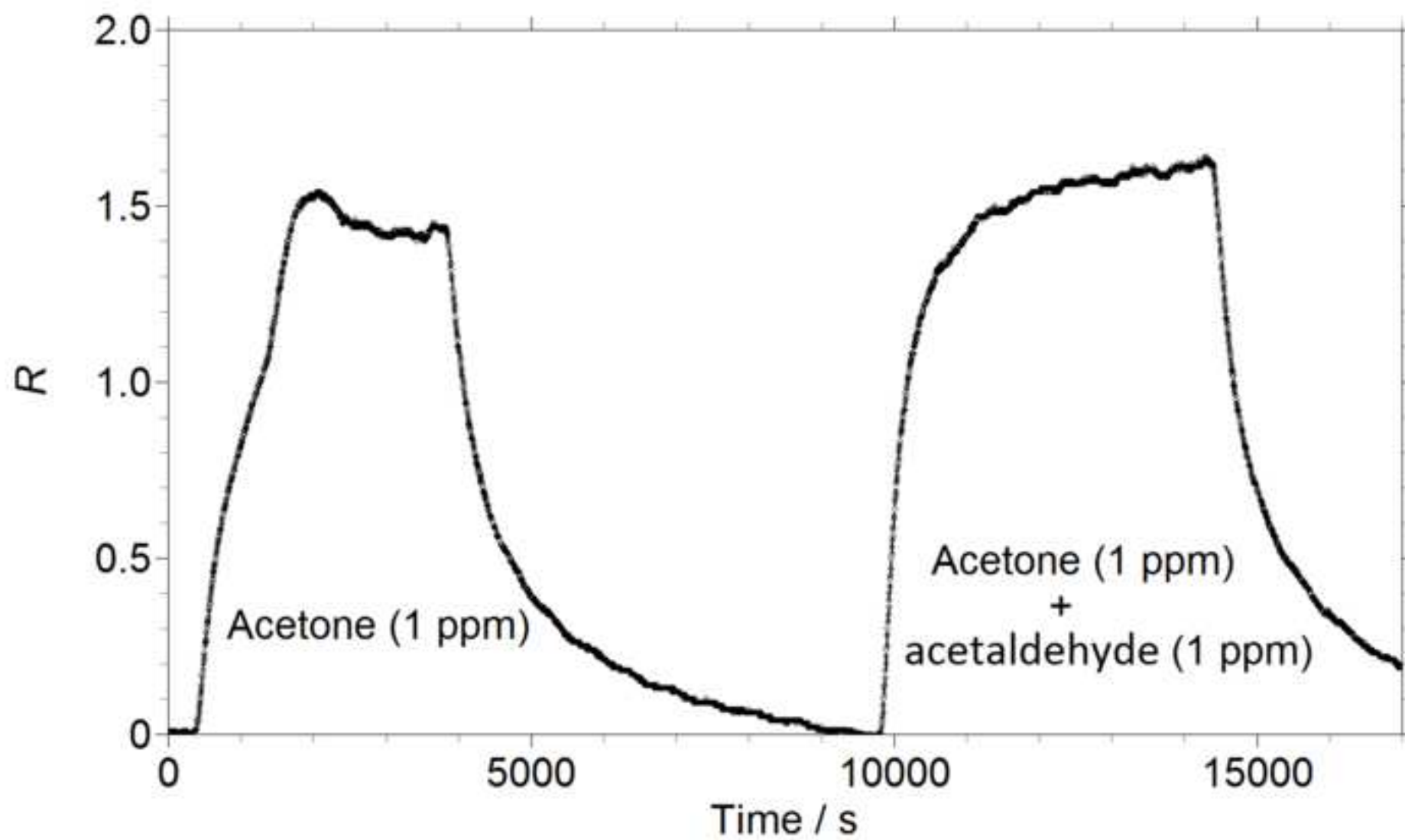


Figure 8

