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Title: Chemoresistive properties of photo-activated thin and thick ZnO films

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Abstract: Room temperature operation is an extremely valuable goal in gas sensing research. Among the metal-oxides that have shown various chemoresistive properties, zinc oxide plays an important role as a wide gap semiconductor (Eg = 3.37 eV) whose chemical activity at surface can be enhanced by proper electromagnetic radiation. This property is fundamental to design gas sensing devices able to operate at room temperature. In this work, nanosized zinc oxide powder was synthesized by sol-gel technique through two different routes. After structural and morphological characterization, the materials were deposited onto miniaturized alumina substrates; one as a thick film by screen printing technique the other one as a thin film by spin coating. The response to nitrogen dioxide was deeply investigated as an important gas target in air monitoring for human safety. Once identified the optimal activation energy for the as-prepared devices, the two types of gas sensors were tested in photo-activated mode with UV-LED of 385 nm peak wavelength. In order to collect information on the role of oxygen coverage in NO2 sensing mechanism with ZnO, thin and thick films were tested in air and in nitrogen conditions. Finally, measurements with several gases were performed in air conditions to compare the performances of thin and thick films. The manufactured sensors resulted suitable for alcohols detection, and thick films yielded negligible responses in comparison with their thin films counterpart. We interpreted this evidence in terms of extinction length of light in ZnO.

***Response to Reviewers**

Response to the Editor

Editor:

Dear Barbara Fabbri:

Reviewers have now commented on your paper. You will see that they are advising that you revise your manuscript.
For your guidance, reviewers' comments are appended below.
If you decide to revise the work, please submit your revision by May 04, 2015, otherwise your paper will be automatically rejected. Please submit a list of changes or a rebuttal against each point which is being raised when you submit the revised manuscript.
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Yours sincerely,

Prof. Ralf Moos
Editor
Sensors & Actuators B: Chemical

Authors:

Dear Editor,

thank you for your letter and to the reviewers for their useful comments. We replied to all questions and considerations and integrated all modifications in the new manuscript, highlighted in yellow color.

In particular, we carried out an addition measurement by using a LED with wavelength of 365 nm thank to Mr Paolo Bernardoni, now included as author in the paper. This new tests were useful for replaying to point 3 of Reviewer #1 comments regarding the lack of reversibility at low energies for ZnO thin films tested with 5 ppm of NO_2 (Figure 3a), a point which was, not sufficiently investigated in the first version of the article.

We look forward to receiving your response.

Best regards,

Dr. Barbara Fabbri

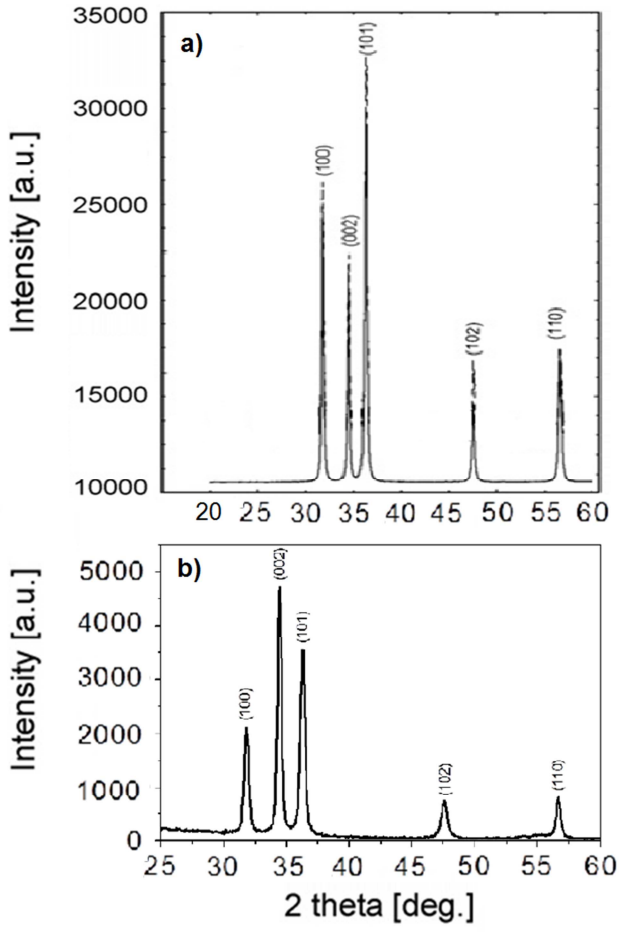
Response to the Reviewer #1

Reviewer #1: MAJOR REVISION
The authors focus on the room temperature operation of metal oxide based gas sensors, which are commonly suffered from excessively high working temperature, through a UV photo-activated mode. Moreover, the contribution of improved gas-sensing performance of thin ZnO film was also discussed in terms of activation energy, and (0001) polar surface. Some valuable experimental results are provided and the discussions are well documented, thus I recommend publication of this manuscript in Sensors and Actuators B: Chemical, after addressing the following points.
Recommendation: accept after Major Revision
Some specific comments are:
1. Section 2.1.1: Why the XRD and SEM analysis were operated with different equipments?

A: XRD and SEM analysis were performed on the ZnO powders and films, respectively. The zinc oxide used to prepare screen-printable paste deposited as thick films, called ZnO-T, was synthetized at Sensor and Semiconductors Laboratory of Ferrara. On the contrary, the zinc oxide used for spin-coated films, called ZnO-t, was synthetized at Department of Industrial Engineering of Padova. Therefore, the morphological and structural characterizations were performed in two different laboratories with different equipments.

2. Lines 15-16 of page 4: "Diffraction patterns were collected over the range 10-120° (2<theta>) with…" However, the pattern was not fully presented in Fig.1(a).

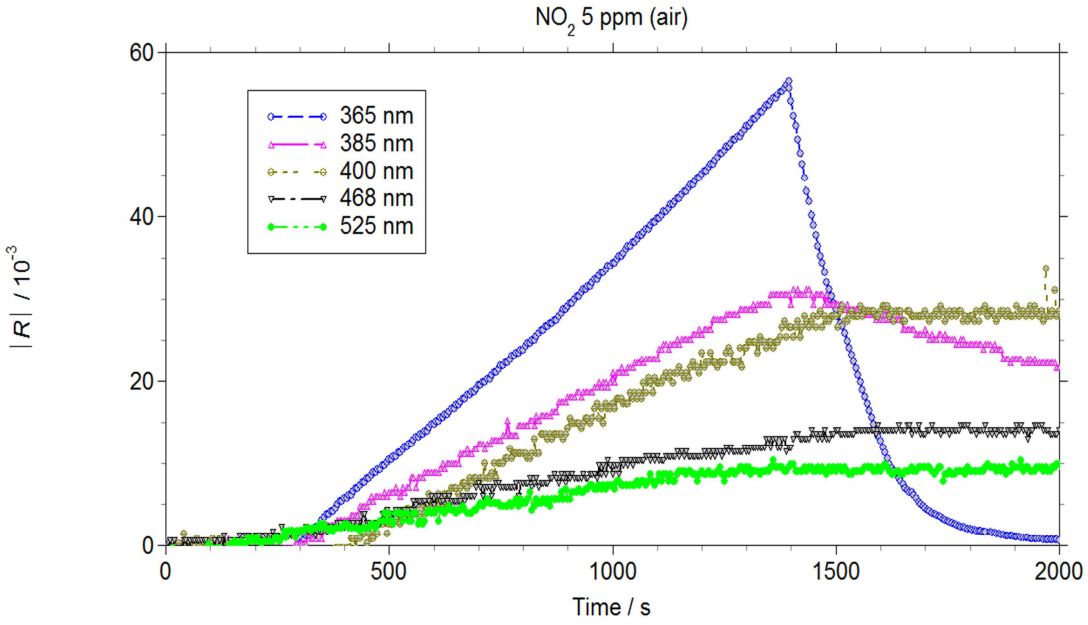
A: We agree with the reviewer about the inconsistency between the statement "Diffraction patterns were collected over the range 10-120° (2<theta>) with…" and the pattern showed in Fig. 1(a). Since the pattern in Fig. 1(b) presents a data collection up to 60° [2 theta], due to some technical problems occurred during XRD measurements, we decided to interrupt also the pattern in Fig. 1(a) at 60° [2 theta] as showed below, in order to present a worthwhile comparison.



Therefore, also the sentence referred to Fig. 1(a) has been changed in "Diffraction pattern was collected at room temperature with steps of 0.02° and dwell time of 10 s. XRD data were elaborated using a Rietveld analysis software [25]."

3. Fig.3(a): The ZnO thin film activated by 385 nm UV light shows the best recovery behavior. Why it almost did not show recovery behavior while being excited by visible lights with longer wavelength?

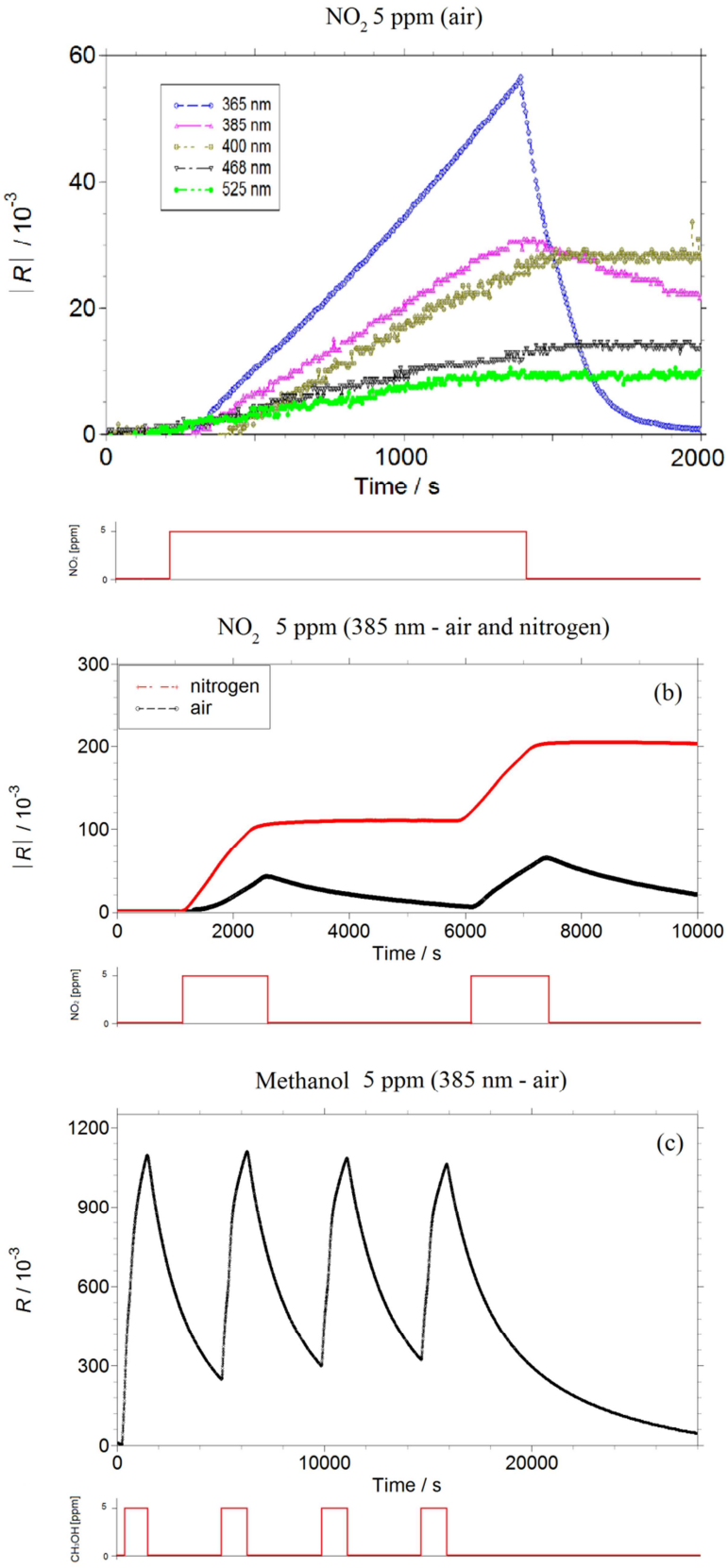
A: We agree with the reviewer about the necessity to explain more in detail the lack of reversibility in the case of longer wavelengths. First of all, based on the wavelength-dependent behavior in photo-activated mode proposed in Reference [23], it is clear that the excitation by radiations with lower energies than the semiconductor bandgap does not result to be efficient to create electron-hole couples, as discussed in the manuscript. This means that a lower number of holes are pushed on the surface where they annihilate electrons of adsorbed oxygen atoms, then the response is lower than that obtained by exciting with radiation of energy equal to bandgap.
Moreover, since the oxidizing behavior of NO_2 on semiconductor's surfaces is a well-established fact, it is reasonable to think of NO_2 interacting with the surface of ZnO via chemical bond. It's very interesting noticing that the energy demand for the excitation of the NO_2 molecule (M. F. MERIENNE, A. JENOUVRIER and B. COQUART, "*The NO_2 Absorption Spectrum. I: Absorption Cross-Sections at Ambient Temperature in the 300-500 nm Region*", Journal of Atmospheric Chemistry 20: 281-297, I995, K. Yoshino, J.R. Esmond, W.H. Parkinson, "*High-resolution absorption cross section measurements of NO_2 in the UV and visible region*", Chemical Physics 221 (1997) 169-174, introduced as [31,32] in References list) is close to that chosen for experimental measurements with ZnO sensors (λ = 385 nm). That excitation destabilizes the bond, increasing the desorption probability. Therefore, this particular radiation causes an increase of ZnO/NO_2 reactivity, both for adsorption and for desorption.
In order to support this explanation regard to the lack of recovery for excitations with higher wavelengths (lower energies), an additional measurement was performed by using a radiation with shorter wavelength than the bandgap. Thus, by applying the same conditions as for the other photo-activated NO_2 measurements, the conductance variation of ZnO thin films was recorded by means of a LED with wavelength of 365 nm and the result has been added to Figure 3a,reported below, that shows tests with NO_2 under illumination with different wavelengths.



Anyway, the radiation wavelength chosen for further investigations on sensing properties was 385 nm. Indeed, even though measurements performed by using 365 nm resulted both in higher response/recovery times and in higher response value than the former, as shown in the previous figure, the diode with wavelength of 365 nm was damaged during the recovery in dry conditions (around 2000 s). This is the reason because the figure presented here does not end at 4000 s as that reported in the first version of the paper.

4. Fig.3: The gas-sensing test eis suggested to be described in detail, especially the light on-off and gas in-out cycles.

A: We agree with the referee, for this reason we modified Fig. 3 to make explicit the gas injection. In particular, under each graph, we included the respective square function.



Concerning the light on-off, we specified in Section 2.1.2 and in the caption of Fig. 3 that, during the gas measurements, the sensors were under continuous illumination. These modifications are reported as follows:

- in section 2.1.2:

The films sensing properties of the films were investigated in a gas-flow chamber, continuously illuminating the surface of each film with LED light sources with wavelengths ranging from 365 to 525 nm.

- caption of Figure 3:

Gas measurements with thin films under continuous illumination: a) NO2 with different wavelengths, b) NO_2 in air and nitrogen conditions, and c) dynamic response to methanol. Below each graph, the respective gas in-out cycles are reported ad a square function.

Therefore, we modified also the following sections in order to clarify how the different measurements were carried out.

- In section 3.2.1:

The sensors were first stabilized in dry conditions under continuous illumination under different radiations wavelengths (365 nm, 385 nm, 400 nm, 468 nm, 525 nm). Thus, since the response time for ZnO sensors in photo-activation mode at room temperature is quite long, we chose a standard NO_2 exposure time of 25 minutes.

- In section 3.2.2:

Nitrogen dioxide measurements were performed in nitrogen and in air conditions, under continuous illumination, to acquire information about the role of adsorbed oxygen in the NO_2 sensing mechanism.

- In section 3.2.3:

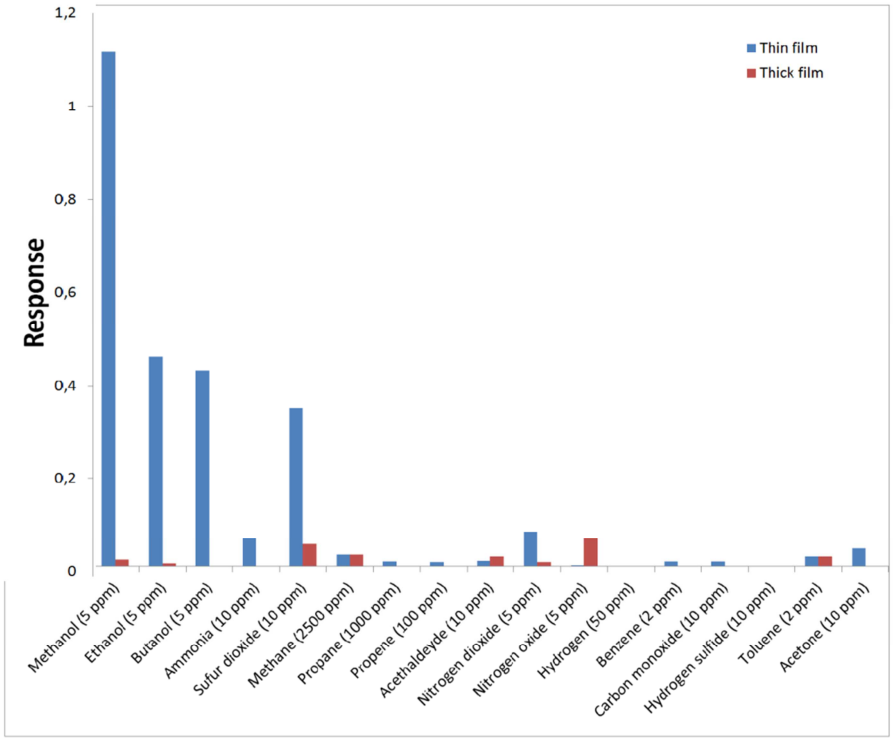
Finally, a comparison between thin and thick films was performed by comparing the responses to several gases obtained in dry conditions and photo-activation modes (λ = 385 nm).

5. Reference [33]: "Material Sciences and Applications" should be changed to "Materials Sciences and Applications".

A: We changed the Reference [33] (which has now changed in [35]) according to the referee‘s suggestion.

6. Fig.4: Some spelling errors should be corrected: "NH3", "SO2", "NO2" and "H2S".

A: We corrected the spelling errors according to the reviewer’s suggestion, substituting the chemical formula with the complete nomenclature in Figure 4, showed below.



Response to the Reviewer #2

Reviewer #2: MINOR REVISION
This paper describes a synthesis process of nanosized zinc oxide powder synthesized by sol-gel technique in two different processes, and characterization of their morphology and sensing properties. The used methodology for the synthesis and characterization is clear and it is easy to follow. Results and discussion are congruent and agree with the presented conclusions. The topic is interesting for some readers in material sciences and deserves publication in Sensors & Actuators: B. Chemical. However, before its final acceptance, some minor revisions are required.

1. The authors should add more statement of the response time and recovery time of the NO_2 sensors.

A: Since the response time for ZnO sensors in photo-activation mode at room temperature is quite long, we choose a standard gas exposure time of 25 minutes because after this time a remarkable change in the slope of the response of all sensors has been observed. The recovery time was already discussed and specific statements were already included in the text.

2. The thin film shows far better performance respect to thick films, because it does not allow the radiation to fully penetrate into the thick films. So it is unnecessary to compare their selectivity further in Fig. 4.

A: The scope of this work was to study the sensing properties of thin and thick nanostructured ZnO films in photo-activation mode. Then, once determined the optimal operating wavelength, we wanted to compare the response of these two type of sensors testing several gaseous compounds in order to identify a possible sensitivity at least for one of them. Two possible interpretations were identified, as reported in section 3.2.3, but that based on the extinction length of light in ZnO was considered the most likely explanation. Then, it has been declared both in section 3.2.3 and in conclusions. Since in the literature the function of light extinction length in chemoresistive sensing mechanism was hardly investigated, we consider worthwhile to report a detailed comparison (Fig.4) between thin and thick films performances. Moreover, seeing as the better performance of thin films in NO_2 preliminary measures did not presume their particular sensitivity to alcohols, the results reported in Figure 4 highlight this further important feature of ZnO thin films.

Research Highlights

- The properties of ZnO thin and thick films photo-activated were deeply investigated.
- The results were interpreted in terms of extinction length of light in ZnO.
- ZnO thin films resulted suitable for alcohols detection at room temperature.

Chemoresistive properties of photo-activated thin and thick ZnO films

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Abstract

Room temperature operation is an extremely valuable goal in gas sensing research. Among the metal-oxides that have shown various chemoresistive properties, zinc oxide plays an important role as a wide gap semiconductor (E_g = 3.37 eV) whose chemical activity at surface can be enhanced by proper electromagnetic radiation. This property is fundamental to design gas sensing devices able to operate at room temperature. In this work, nanosized zinc oxide powder was synthesized by sol-gel technique through two different routes. After structural and morphological characterization, the materials were deposited onto miniaturized alumina substrates; one as a thick film by screen printing technique the other one as a thin film by spin coating. The response to nitrogen dioxide was deeply investigated as an important gas target in air monitoring for human safety. Once identified the optimal activation energy for the as-prepared devices, the two types of gas sensors were tested in photo-activated mode with UV-LED of 385 nm peak wavelength. In order to collect information on the role of oxygen coverage in NO_2 sensing mechanism with ZnO, thin and thick films were tested in air and in nitrogen conditions. Finally, measurements with several gases were performed in air conditions to compare the performances of thin and thick films. The manufactured sensors resulted suitable for alcohols detection, and thick films yielded negligible responses in comparison with their thin films counterpart. We interpreted this evidence in terms of extinction length of light in ZnO.

Keywords: ZnO, thin films, thick films, photo-activation, room temperature

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1. Introduction

Room temperature operation is an issue for intrinsic safety of sensors working in harsh or industrial environment, moreover it is interesting to the power consumption and consequently the size of its associated electronics [1-3]. Nowadays, solid-state devices have evolved rapidly by improving the quality and decreasing the processing and operating costs [4]. From this point of view, metal-oxide gas sensors represent a reference thanks to their attractive features such as fast and reverse response, high sensitivity, low costs of manufacturing and small dimensions. These important characteristics allow a suitable integration for different uses making gas sensors fundamental in several fields, such as environmental monitoring, medical diagnoses, safety systems and industrial process control [5-9]. The design of a gas sensor includes different steps, such as the integration of functional materials with sensors substrates. Deposition technology is one of the basic aspects to take into account in the design of these devices. In particular, it is important to deeply understand the relationships between the physical-chemical properties of the materials and their possible applications. A huge number of parameters have to be considered: thermal effects, chemical reactions with other components, flexibility, uniformity and thickness [4]. Since the sensing mechanism of metal-oxide gas sensors relies on variations of the electrical resistance, due to the interactions of the functional material with oxygen and gas molecules at the surface, it is fundamental to know the dimensions of both the grains and the film to compare them with the length scale of surface interactions. For the majority of metal-oxide semiconductors, the variation of a film electrical resistance induced by bulk/surface charge transfer is promoted by heating at nominal temperatures [10-12]. Despite the significant performances of these devices, thermal-activation entails high power consumption, lower durability and safety risk in presence of flammable gases. Photo-activation mechanism represents a precious alternative to achieve room temperature gas sensing [13-15].

Among the metal-oxide semiconductors employed in gas sensing, many authors have paid attention to ZnO due to its properties as photo-activated material, in particular to UV radiation [16-

21]. In fact, thanks to its high exciton binding energy (60 meV), ZnO crystals are characterized by an efficient excitonic emission at room temperature [22].

In this work, ZnO films, prepared following two different syntheses, were first tested with NO_2 to investigate the dependence of sensitivity vs. the radiations wavelengths. The excitation wavelength that gave the best results was the closer to ZnO bandgap (λ = 385 nm), in agreement with [23]. Then, we examined the conductance variations induced by NO_2 dispersed in either in nitrogen or in air conditions, in order to understand the influence of surface configuration on the sensing mechanism. Finally, we compared the behavior of thick and thin ZnO films tested with several gases by exposure to UV-LED.

2. Material and methods

2.1. Thick films

ZnO powder employed for thick film deposition (ZnO-T) was prepared by means of a classical sol-gel route. A proper amount of $Zn(NO_3)_2 \cdot 4H_2O$ was dissolved in doubly distilled water. The pH of the solution was brought to 7.5 by drop-wise addition of ammonium hydroxide solution (25%). The reaction mixture was stirred for 1 h and then kept at room temperature for 24 h. The product was washed several times with water, vacuum-filtered and dried at 80 °C overnight, then calcined at 450 °C for 2 h, the temperature being determined from TG/DTA analysis. The yield of the reaction was around 90%. Obtained powders were screen-printed onto suitable alumina substrates, equipped with pre-deposited electrodes for the measurement of the film's resistance. The thickness of the depositions was about 30 μm, then the films were then fired in a muffle oven at 750°C for 1 h [18, 20].

2.2 Thin films

The synthesis of ZnO powder for thin films depositions (ZnO-t) was also prepared by sol-gel technique. A 0.5M ethanolic solution of Zinc Acetate dehydrate was prepared and monoethanolamine was added dropwise under constant stirring, keeping unitary the ratio between

the metal ion and the amine. After 1 hour stirring, the thin film was deposited by spin-coating at 2000 rpm for 30 seconds on the same alumina substrate employed for the thick film deposition. Film thickness was measured by means of ellipsometry and resulted about 250 nm. Thin films were thermally stabilized in air at 100°C for 10 minutes and then the spinning/stabilization procedure was repeated up to 4 times. The films were subjected to a final annealing at 500°C for 1 hour in air [24].

2.2 Characterization of the films

2.1.1 Structural and morphological characterization

The crystalline phase of the powders for the thick film depositions was investigated by X-Ray Diffraction (XRD) using a PhilipsPW 1830 vertical diffractometer with Bregg-Brentano geometry (Cu Kα radiation, 40 kV, 30 mA) provided with a graphite monochromator. Diffraction patterns were collected at room temperature with steps of 0.02° and dwell time of 10 s. XRD data were elaborated using a Rietveld analysis software [25]. The morphology of the films was observed using scanning electron microscopy (SEM, Carl Zeiss, model EVO 40).

Thin films were characterized by XRD by using a Philips PW1710 diffractometer equipped with glancing-incidence X-Ray optics. The analysis was performed at 0.5° incidence using CuKα Ni-filtered radiation at 30 kV and 40 mA. The microstructure of the films was investigated with a Zeiss-Gemini LEO 1530 Field Emission Scanning Electron Microscope (FE-SEM).

2.1.2 Gas sensing measurements

The films sensing properties of the films were investigated in a gas-flow chamber, continuously illuminating the surface of each film with LED light sources with wavelengths ranging from 365 to 525 nm. Gases were from certified bottles and pure gases were admixed and fluxed through mass-flow controller. Several gases were tested, in order to obtain a wide overview of the sensing behavior of the nanosized material and highlight the differences between thick and thin films. Table

I reports the gases and the concentrations, the latter being chosen on the bases of the Threshold Limit Values (TLV) [26, 27], also reported in the table. In the case of alcohols we focused on concentrations strongly below the TLVs, whereas for the others compounds we used concentrations of the same order of magnitude of TLV, except for the case of acetone, for which we choose half of the odor threshold, that is 50 times lower than TLV.

3. Results and discussion

3.1 Structural and morphological characterizations

XRD patterns showed a hexagonal wurtzite structure both for ZnO-T and ZnO-t powders. By observing the peaks intensity for each spectrum, one can notice that ZnO-T is dominated by (101) peak (see Fig. 1a), whereas ZnO-t is dominated by (002) peak (see Fig. 1b). This means that ZnO-t was grown in good alignment with *c*-direction, then its high diffraction intensity ratio of (002) polar planes to (100) nonpolar plane indicates a large fraction of polar planes to a large extent, hence there are more structures with their *c* direction normal to the substrate than for ZnO-t powder. Indeed, ZnO is a crystal with a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the *c*-axis. Moreover, ZnO is characterized by polar-nonpolar surfaces and the morphologies can be identified from the relative amount of them. The oppositely charged ions produce a positively charged plane (0001) which ends with zinc, and a negatively charged plane $(000\bar{1})$ ending with oxygen, which compose polar surfaces resulting in a normal dipole moment and spontaneous polarization along the *c*-axis, as well as a divergence in surface energy. The $(01\bar{1}0)$ plane represents the nonpolar plane. The morphology of the exposed surface can be tuned by controlling the growth environment of ZnO nanostructures. In fact, such a structure causes a divergence in the surface energy of (0001) polar surface and a strong anisotropy in the growth rate. Thus, wurtzite-type ZnO usually tends to minimize the exposed areas of (0001) polar facets, which possess high surface energy, and maximize the exposed areas of the $(01\bar{1}0)$

nonpolar facets [16, 22, 28-29]. The Debye-Scherrer formula was used to estimate the crystallite size of as grown powders of 40 nm for ZnO-T and 29 nm for ZnO-t. SEM analysis revealed a similar morphology, round-shape nanoparticles, both thick and thin sensing layers (see Fig. 2a, 2b). The annealing temperature could affect the growth of ZnO crystalline grains; ZnO-T was annealed at 750 °C whereas ZnO-t at 500 °C, this may have led the difference in grains dimensions. In summary, the morphology of ZnO thick films suffers from the grain coalescence more than in ZnO thin films.

3.2 Photo-activated ZnO gas sensing properties

Gas sensing qualification consisted of measuring the conductance variations vs. gaseous analytes. Results were evaluated on the basis of the following definition of response:

$$R = \begin{cases} \left(G_{gas} - G_{air}\right)/G_{air} & \text{for a conductance increase (reducing gas)} \\ \left(G_{gas} - G_{air}\right)/G_{gas} & \text{for a conductance decrease (oxydizing gas)} \end{cases}$$

which implies, in the case of *n*-type semiconductors, a positive (negative) response to reducing (oxidizing) gases and a negative response to oxidizing gases; the opposite holds for *p*-type semiconductors.

3.2.1 NO_2 measurements with different wavelengths

Before carrying out measurements in photo-activated mode, it was necessary to identify the best excitation wavelength to optimize the sensor performance. To this aim, we performed tests with NO_2, due to its importance in gas sensor research and in particular about ZnO films [18, 30]. The sensors were first stabilized in dry conditions under continuous illumination under different radiations wavelengths (365 nm, 385 nm, 400 nm, 468 nm, 525 nm). Thus, since the response time for ZnO sensors in photo-activation mode at room temperature is quite long, we chose a standard NO_2 exposure time of 25 minutes. In Fig. 3a, the absolute value of the response of thin film a ZnO thin sensor to 5 ppm of NO_2 is showed at different irradiation wavelengths (thick film results are not reported because of negligible responses). It should be noticed that an increase of the photon energy results in an increase of the response, as well as in a shorter recovery time, indeed, when

illumination wavelength is set at 365 and 385 nm the response is reversible, whereas at longer wavelengths the response seems to be irreversible. In this way, the behavior over (365 nm) and under (385 nm) bandgap (E_g = 370 nm) was studied. The response/recovery times and the response intensity, illuminating ZnO thin film with 365 nm, resulted even higher than those obtained with just under (385 nm) bandgap energy (Fig. 3a). The evident faster kinetics observed can be probably interpreted in terms of more energetic radiation that improves the efficiency of semiconductor activity.

The physical reason for a wavelength-dependent behavior in photo-activated conductometric gas sensor is proposed in [23], where it is showed that, in the case of CdS, a material with similar characteristics, the maximum of the response is found at the bandgap energy. Since the bandgap energy of ZnO corresponds to a wavelength of about 370 nm [18, 20, 21], the obtained results are consistent with the above-mentioned model. Concerning the lack of reversibility at low energies, excitation wavelengths significantly longer than the bandgap do not efficiently create electron-hole couples. As a consequence, very few holes can be dragged by the electric field toward the surface, where they would annihilate electrons trapped in surface states, resulting in desorption processes and the restoration of the conductance level. Moreover, since the oxidizing behavior of NO_2 on semiconductor surfaces is a well-established effect, it is reasonable to think that NO_2 interacts with the surface of ZnO via chemical bond. It is also very interesting to observe that the energy demand for the excitation of the NO_2 molecule [31,32] is close to the energy of the photons in the irradiation experiment (λ = 385 nm). Excitation destabilizes the bond, increasing the desorption probability. Therefore, this particular radiation causes an increase of ZnO/NO_2 reactivity, both for adsorption and for desorption. On the basis of these results, we performed the entire set of gas measurements with the LED at λ = 385 nm.

3.2.2 NO_2 sensing in nitrogen and in air conditions

Nitrogen dioxide measurements were performed in nitrogen and in air conditions, under continuous illumination, to acquire information about the role of adsorbed oxygen in the NO_2 sensing

mechanism. The result is showed in (Fig. 3b). It can be noticed that in nitrogen the response is irreversible, whereas in air it is reversible, even if less intense. This result sheds light on the gas-surface interaction. As NO_2 molecule approaches the surface, it is reduced to NO due to the weakness of the N-O bond, oxidizing the surface. As soon as NO_2 is removed in air, the process proceeds backward; in nitrogen, however, the surface coverage of oxygen is very poor, in turn, the desorption process hardly proceeds.

3.2.3 Thin and thick UV-activated films

Finally, a comparison between thin and thick films was performed by comparing the responses to several gases obtained in dry conditions and photo-activation mode at $\lambda = 385$ nm. Results of gas sensing measurements in the case of thick and thin ZnO films were very different. For all the tested gases, the responses of thick films resulted negligible in comparison with those of thin films, with high signal-to-noise ratios. In Fig. 3c, the dynamic response of a thin sample is showed as a function of time in the case of methanol, the gas for which best performance was recorded. Despite the device did not reach a steady state during the 20 minutes of the measurement, a very good repeatability can be inferred.

The absolute values of the responses to all the tested gases for both thin and thick samples are reported in Fig. 4. Besides the negligibility of the responses of thick films for all gases, an important feature arose in the case of alcohols, that is, the response decreases with the length of the alcoholic chain. The other gases resulted in a much lower response, except SO_2, to which the film responded similarly to ethanol and n-butanol. However, in the latter case it is worth to be stressed the high concentration we used (5 times the TLV).

The negligible response of thick films could be ascribed to different reasons. On the basis of the analysis of XRD patterns, ZnO-t powder is dominated by polar planes. From the literature, it is known that they generate more easily oxygen vacancies, but it has been also observed that the higher the defect density the higher the chemical reactivity [28, 33], this suggesting a more efficient sensing mechanism for the phase of ZnO-t films. Subsequently, the bulk conductance was evaluated

for both film types with the method of temperature jumps [34]. This technique neglects quantum mechanical tunneling, but it is an easy way for an approximate estimation. Measurement was performed at 250 °C, for the bulk conductances resulted of the order of tens of nS for both films, and the energy barriers 0.6-0.7 eV. Despite this, the extinction length of light in the material plays a crucial role, indeed, for photons with wavelength λ = 385 nm, the extinction length in ZnO is of the order of 1 μm [35, 36]. Therefore, only a small fraction of the thick film is involved by photoconductance and photo-activation of surface chemistry. Among the features that improve the response of ZnO we have investigated, i.e. the structural differences and the extinction length of light, the latter appears to be the most plausible explanation.

Conclusions

Zinc oxide powders have been synthesized via different routes and deposited as thick and thin films. XRD analysis on these powders highlighted a significant difference in diffraction ratio between the peaks associated to the polar and nonpolar planes, whereas SEM investigation showed round-shape nanosized particles in both cases. Both types of films were tested with NO_2 by using different LEDs as light sources, the best excitation wavelength resulted the closer to the band gap energy of ZnO. Further NO_2 measurements carried out with nitrogen as carrier, to investigate on the role of adsorbed oxygen in the sensing mechanism, have shown an enhancement of the response together with an irreversibility of the signal that can be associated to the lowered oxygen surface coverage. The comparison between the thick and thin films, based on measurements with several gases, has shown a far better performance for thin films. A possible explanation is the extinction length of light in ZnO, which does not allow the radiation to fully penetrate into the thick films.

Acknowledgements

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Figure captions

Fig. 1: XRD patterns of a) ZnO-T powder, b) ZnO-t powder.

Fig. 2: SEM micrograph of a) ZnO-T film, b) ZnO-t film.

Fig. 3: Gas measurements with thin films under continuous illumination: a) NO_2 with different wavelengths, b) NO_2 in air and nitrogen conditions, and c) dynamic response to methanol. Below each graph, the respective gas in-out cycles are reported ad a square function.

Fig. 4: Responses to all the tested gases for both thin and thick films.

Table(s)

Table I. Tested gases and respective concentrations.

Gas	Methanol	Ethanol	N-butanol	NH_3	SO_2	Propane	Propene	NO_2	Hydrogen	Benzene	CO	H_2S	Acetone
Concentration [ppm]	5	5	5	10	10	1000	100	5	50	2	10	10	10
TLV [ppm]	200	1000	20	25	2	2500	500	1	/	0.5	25	10	500

Figure(s)

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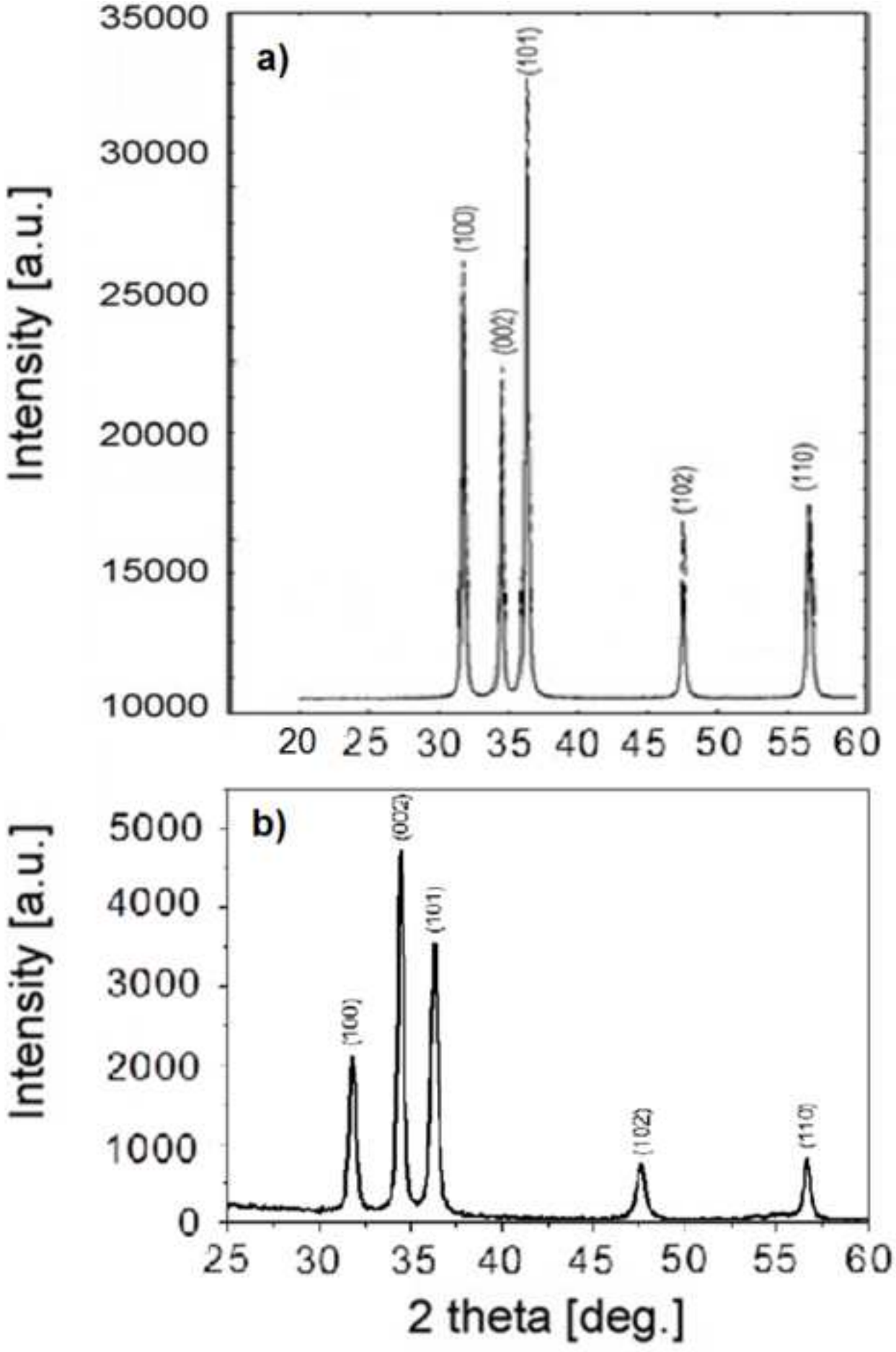

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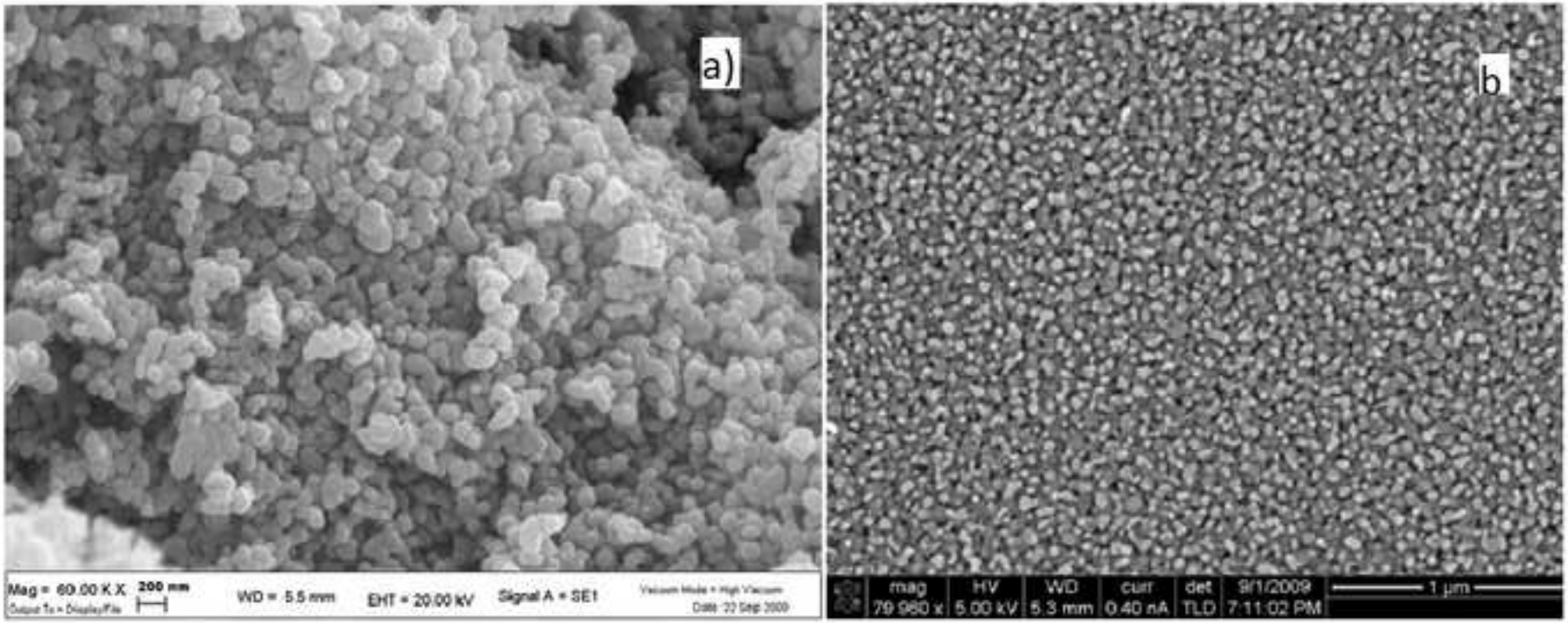

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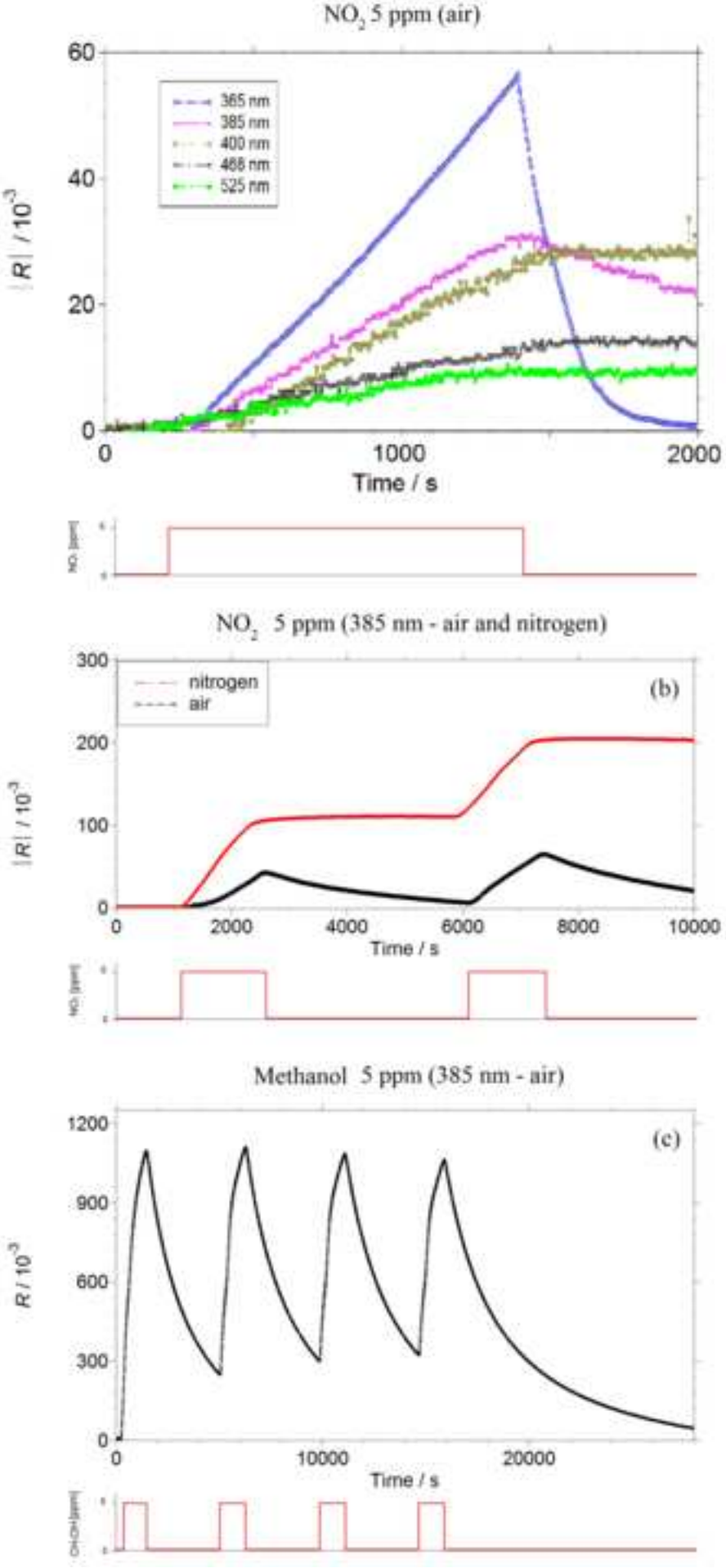

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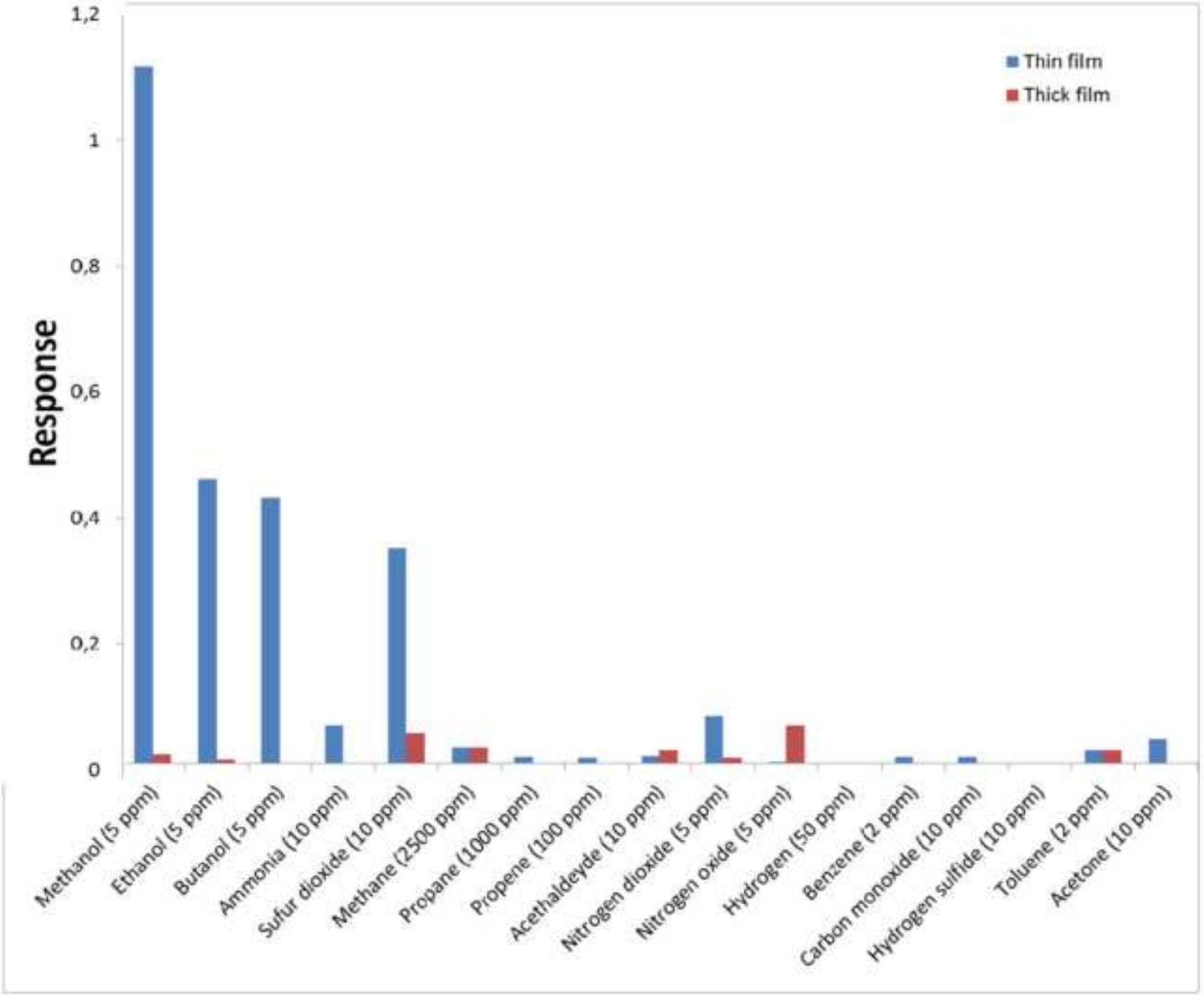

Supplementary Material

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***Author Biographies**

Authors Biography

Barbara Fabbri She obtained her master degree in Physics at University of Ferrara in 2011 and its PhD in Physics in 2015 at the same University. Currently she is a PostDoc researcher involved in the field of gas sensors and micromachining.

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.

Andrea Gaiardo He obtained his Degree in Chemistry at the University of Ferrara in2011 and the Master's Degree in Chemical Sciences at the University of Ferrara in2013. 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.

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 top ractical 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.

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 themodeling of transport phenomena in nanostructured semiconductors.

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 volatileorganic compounds (VOCs) of medical interest. With her team she won Unife Cup2013, a business plan competition that rewards innovative start-ups and StartCup 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.

Sandro Gherardi Bachelor in Physics Technologies at the University of Ferrara in2002. 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.