Sensors and Actuators B 179 (2013) 107–113

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Preparation of nitrogen doped TiO_2 nanofibers by near field electrospinning (NFES) technique for NO_2 sensing

F. Ruggieri [a], D. Di Camillo [a], L. Lozzi [a], S. Santucci [a], A. De Marcellis [b], G. Ferri [b], L. Giancaterini [b], C. Cantalini [b,*]

[a] Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio 67100, L'Aquila, Italy
[b] Department of Industrial and Information Engineering and Economics, University of L'Aquila, Via Gronchi 18, Nucleo Industriale di Pile, 67100 L'Aquila, Italy

ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 11 October 2012
Accepted 18 October 2012
Available online 29 October 2012

Keywords:
Near field electrospinning
Nanofibers
Titanium dioxide
Resistive gas sensor
Integrated sensor interface
CMOS technology

ABSTRACT

Parallel arrays of well aligned crack-free N-doped and undoped TiO_2 nanofibers (3–4 mm long, 300–500 nm diameter) have been deposited by near field electrospinning (NFES) technique on Si_3N_4 substrates with interdigitated Pt electrodes and annealed at 400 °C for 1 h. Anatase TiO_2 with crystallites' size of approximately 12 nm have been prepared and characterized by XRD, SEM, TEM and XPS techniques. Experimental measurements have been conducted through an ad hoc analog integrated resistive sensor interface, based on an oscillating circuit, fabricated in a 0.35 μm standard CMOS technology. Gas response to NO_2 in the range 1–10 ppm and 100–300 °C operating temperature (OT) has shown best practical sensor sensitivity ($S = R_G/R_A$) at a relatively low OT (150 °C) and detection limits down to 1 ppm gas. Nitrogen doping at N:Ti 1:1 atomic ratio has been proposed in order to decrease the intrinsic resistance of TiO_2, thus enabling better signal to noise ratio of the electrical response.

1. Introduction

A metal oxide sensor is characterized by a responsive surface and a transduction mechanism, which enables the atomic scale interaction to be transformed into an electrical, optical or mechanical response [1]. Semiconductor metal oxides play a very important role in gas sensing applications considering their ability to adsorb analytes on their surface like NO_2, O_3, H_2, CO, H_2O, etc. The sensor surface interacts with the sensed molecules by physical adsorption or by weak chemisorption often followed by chemical oxidation or reduction of the surface, thus resulting in a change of the physical properties of the material, such as electron density, optical properties or temperature [2]. The specific interaction between the sensor surface and the target gas, resulting in both sensitivity and selectivity of the response, is strictly dependent on its chemical composition, morphology as well as the occurrence of surface defects like metal or oxygen vacancies [3,4].

Since the sensing mechanism is controlled at the molecular level, the use of nano-dimensional materials in sensor devices can bring important benefits in response efficiency. The development of enhanced gas sensors has taken advantage in the last decade, both from the research of new materials [5,6] and from the application of nanotechnologies [7]. Deep investigation of nanostructured materials by the development of nanocomposite [8], hybrid [9] and hierarchical nanostructures [10], is currently one of the most dynamic research issues.

Gas sensor 1D-nanostructures, utilizing nanowires and nanotubes improve the sensing performance, by exploiting the nanofibers' high activity, large specific surface area to volume and small size [11–14]. Among a large variety to prepare 1D nanowires, electrospinning of nanofibers represents one of the most simple and versatile approaches [15–17]. The disorderly fashion of such deposited nanofibers, however, has limited its full potential.

Near field electrospinning (NFES) represent an evolution of the electrospinning technique that enable to electrospun various materials into uniaxially aligned nanofibers opening to the exploration of a range of interesting properties and applications associated with 1D nanostructures [18]. For example one of the possible advantages when utilizing 1D nanostructures as resistive gas sensors, is represented by the suppression of the "porosity factor" of the device, which describes how the device's response (i.e., the resistance change) is attenuated in an actual porous sensing body due to a consumption of the stimulant gas during its diffusion inside [19]. Drawbacks related with the NFES technique, on the other hand, are still represented by difficulties associated with reproducible growth, adhesion of the nanofibers to the substrate and establishing good electrical contacts between the fibers and electrodes to reduce the signal to noise ratio [20,21].

* Corresponding author. Tel.: +39 0862 434233; fax: +39 0862 434203.
E-mail address: carlo.cantalini@univaq.it (C. Cantalini).

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http://dx.doi.org/10.1016/j.snb.2012.10.094

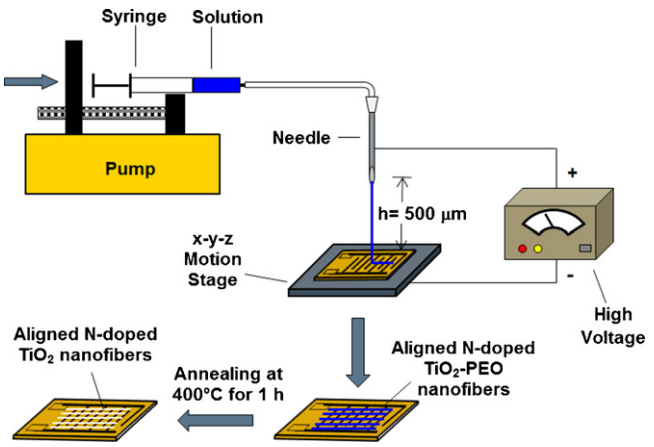

Fig. 1. Near field electrospinning (NFES) apparatus.

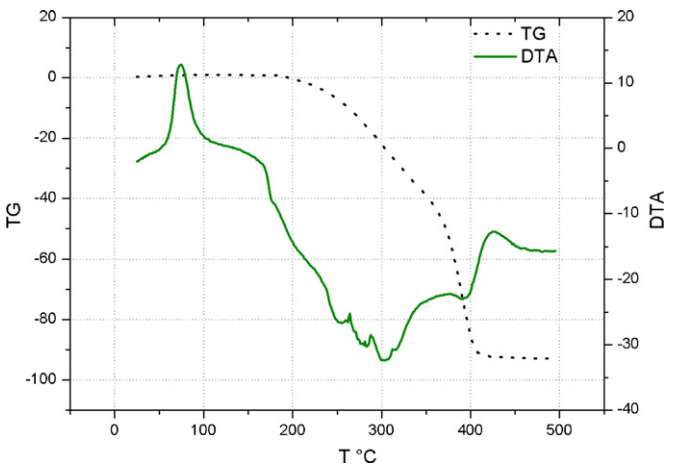

Fig. 2. Thermo gravimetric (TG) plot (dotted lines) obtained by heating the PEO (poly ethylene oxide) at 5 °C/min to 500 °C.

Following previous investigations [18,22,23] this paper reports on the preparation by NFES technique of ID N-doped TiO_2 nanowires as NO_2 gas sensor and on the application of a suitable analog electronic CMOS integrated interface designed for resistive gas sensors [24–28]. Here the Nitrogen doping at N:Ti 1:1 atomic ratio is proposed, following previous research [29,30], to create an acceptor level in the bandgap of TiO_2 which improves both sensor conductivity and signal to noise ratio, whereas the use of a dedicated electronic integrated interface has allowed to optimize, in terms of sensitivity and resolution, the sensor parameter detection considering its baseline and variation range [31].

2. Experimental

The TiO_2 undoped nanofibers were prepared by dissolving in ultrasonic bath 300 mg of polyethylene oxide (PEO M_w = 300,000) in 3480 μl of CH_3CN under vigorous stirring. After stabilizing with 680 μl of glacial acetic acid (AcA 97.7%) 1800 mg of $TiOBu_4$ were added to the PEO base solution and left to stabilize for 8 h under stirring. The TiO_2 doped nanofibers were prepared by the same method as described but adding slowly at the end 177 μl of ethylenediamine (EDA 99.5%) to reach an atomic ratio N:Ti 1:1.

The solution was electrospun by NFES apparatus consisting of: a plastic syringe equipped with a tungsten spinneret of a micrometer tip diameter, a high-voltage power supply, a grounded collector, a *x–y* piezomotor controller and a *z*-stages to control the collector movement. The equipment setup is reported in Fig. 1.

A silicon nitride (Si_3N_4) substrate with Pt interdigital electrodes was utilized to deposit the nanofibers. The solution flux was controlled by a syringe pump and fixed at 20 μl/h. The applied electrostatic voltage was about 1.1 kV. After the deposition, the samples were annealed in an oven for 1 h at 400 °C with a heating rate of 1 °C/min.

Electrical test were carried out by utilizing an analog integrated electronic interface for resistive gas sensors as described in Section 3.2 by exposing the N-doped TiO_2 nanofibers to NO_2 gas (1–10 ppm in dry air), CO and H_2O, in the temperature operating (OT) range of 100–300 °C.

3. Results and discussion

3.1. Microstructural characterization

By attaching the grounded substrate onto precision *x–y–z* robotic stages with the spinneret at a height of approximately 500 μm away from the grounded plate (see Fig. 1), it is possible, as previously reported [32,33], the direct positioning and control of the nanofiber layout pattern. Due to the computer controlled nature of the process, the spatial control of fiber deposition can be programmed to produce customized layout of fibers with average diameters ranging from 200 to 600 nm.

Indeed the ability to truly control the deposition pattern of nanofibers in the electrospinning process depends mainly on the characteristic of solution. The right balance between the solution viscosity and evaporation rate of solvent is necessary to allow the deposition of a stable jet of polymer on substrate. It turns out that the NFES conditions are much more critical than those for the classical electrospinning due to short time of flight and the required higher stability of solution on the tip. Therefore, in NFES deposition it is necessary optimize operating parameters like the voltage applied, polymer feed rate, concentration, polymer molecular weight of the solution, operating temperature, relative humidity, collector type, diameter of the needle and offset distance between the needle tip and collector [34–36].

After the deposition the fibers are composed by titanium precursor embedded in the PEO matrix. Fig. 2 show the thermogravimetric (TG) plot of the PEO when heated up to 500 °C.

Considering the dotted line in Fig. 2, polymer burn out is completed at 400 °C. Annealing at temperatures ranging from 400 to 500 °C for 1 h allows polymer removal as well TiO_2 crystallization. Annealing at these temperatures generally does not determine the breakage of the nanofibers, which still show a continuous structure with the reduction of the nanofiber diameter and the formation of titania crystals.

Fig. 3A shows SEM images of 400 °C annealed TiO_2 nanofibers deposited on silicon nitride substrate with Pt patterned finger type electrodes (vertical light gray stripes). These nanofibers (the horizontal white lines) were deposited when the substrate was moving, with respect to the syringe, following a squared-wave trajectory, with a speed of 50 cm/s. The distance between the different nanofibers was fixed to 50 μm and their length at 4 mm. This method allows the preparation of continuous and well-ordered structures having a length up to several millimeters.

Fig. 3B highlights at higher SEM magnification the shape and the dimension of single nanofiber which results to be continuous, smooth, homogeneous, crack free and with an average diameter of approximately 500 nm. All the fibers resulted to lay down onto the Pt electrodes bridging adjacent electrodes. TiO_2 nanofibers did not peel off from the substrate during handling and resulted to have good adhesion up to 500 °C annealing temperature. This unique morphology, highly advantageous for gas sensors, results in ready

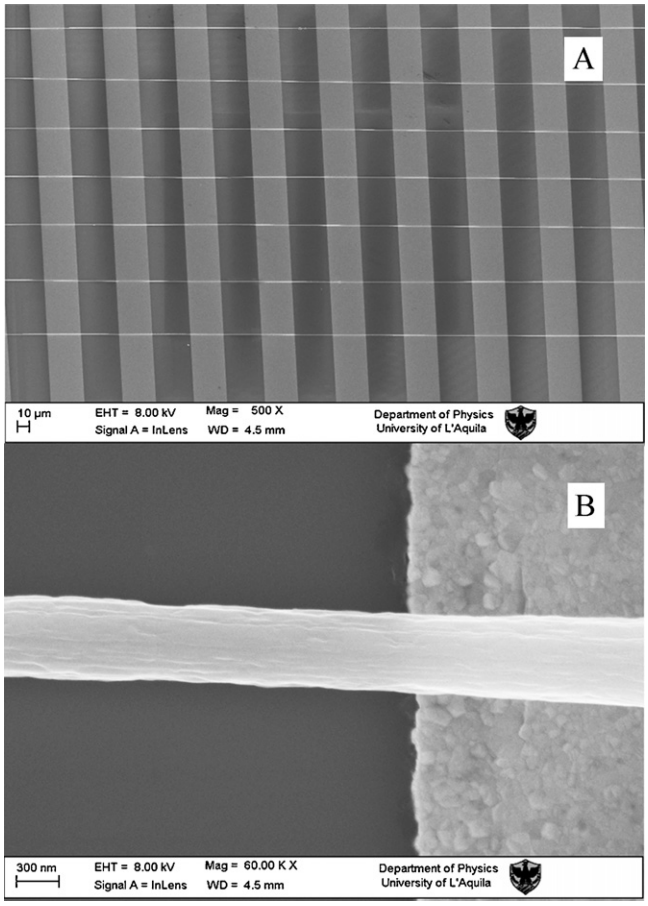

Fig. 3. SEM image of aligned N-doped TiO_2 nanofibers (horizontal white lines) at low (A) and high (B) magnifications on silicon nitride substrate with Pt patterned electrode (gray vertical stripes) after annealing at 400 °C for 1 h. The nanofibers distance is about 40 μm. The average diameter is 500 nm.

gas accessibility to the exceptionally high surface-to-volume ratio of the nano-structure.

High resolution TEM picture of the N-doped TiO_2 after annealing at 400 °C temperature is reported in Fig. 4. The picture shows the development of a fine texture of equiaxially shaped round crystallites with diameter sizes normally distributed (see the inset of Fig. 4) ranging from 11.6 and 13.6 nm size. The reduction of the crystallite size below 10 nm if from one side it increases the base line

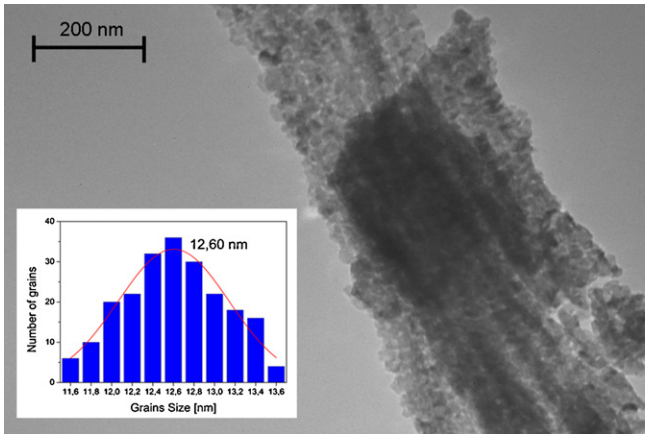

Fig. 4. TEM image of single N-doped TiO_2 nanofiber after annealing at 400 °C for 1 h. The inset shows the crystallites' grain size distribution (12.6 nm is the average crystallite size diameter).

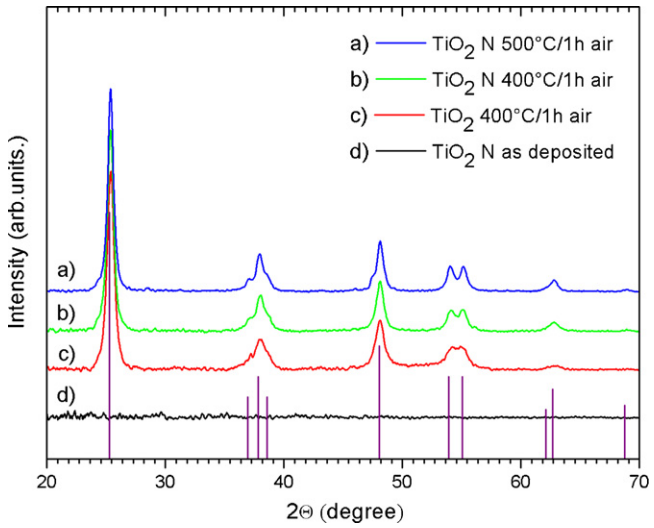

Fig. 5. XRD spectra of N-doped TiO_2: as deposited (d), annealed at 400 °C (b), annealed at 500 °C (a). Undoped TiO_2 annealed at 400 °C (c) for comparison.

resistance (i.e., the resistance in dry air R_A), on the other hand has a positive effect since it increases the practical sensitivity $S = R_G/R_A$ of the sensor [31]. Crystallite dimensions of 12.6 nm average size as here measured by TEM investigation, may represent a reasonable trade off when managing the two contributions.

Fig. 5 shows the XRD spectra of TiO_2 nanofibers annealed at 400 °C for 1 h compared to N-doped TiO_2 nanofibers samples annealed at 400 and 500 °C. XRD spectra were acquired in grazing incidence geometry (incidence angle = 0.2°) to reduce the contribution of substrate. The vertical bars in the figure show the position of the crystalline planes belonging to TiO_2 anatase (ref: JCPDS-ICDD Card No. 21-1272, 1995). The formation and the evolution of crystalline TiO_2 phases resulted neither to be influenced by annealing at 400 °C or 500 °C temperature nor by nitrogen doping. These outcomes were confirmed by comparative parallel XRD measurements, carried out on massive samples prepared by conventional electrospinning technique under the same experimental conditions. The crystallite size of N-doped and undoped TiO_2 nanofibers, were extimated by using the Scherrer equation by the half width of the (1 0 1) plane of the anatase phase. The mean crystalline size resulted to range between 10 and 13 nm, in good agreement with the dimensions obtained by TEM analysis (see the inset of Fig. 4). For these reasons annealing temperature was eventually set at 400 °C and 1 h, in order to yield: complete PEO binder burn out, full TiO_2 anatase crystalline phase formation and to avoid N atoms depletion from the lattice upon heating at higher temperatures (see XPS discussion).

Fig. 6 shows the N 1s XPS signal of the N-doped TiO_2 sample (N/Ti = 1) before (as deposited) and after annealing at 400 and 500 °C. In the figure it is also reported the N 1s signal of undoped TiO_2 annealed at 400° (blank signal). The as deposited N-doped TiO_2 sample shows a quite intense peak of N 1s at about 400 eV, which can be assigned to NO bond or interstitial N atoms in the TiO_2 lattice.

By annealing at 400 °C and increasing the annealing temperature up to 500 °C the N 1s peak intensity decreases. At 500 °C annealing the N signal is strongly reduced, but still higher as compared to the N 1s of the undoped film (here referred as the "Blank signal"). These data suggest that nitrogen atoms are weakly bonded in the TiO_2 cage and eventually can be easily lost upon increasing the annealing temperature. XPS detailed scans of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ lines highlighted the formation of Ti^{4+} with characteristic

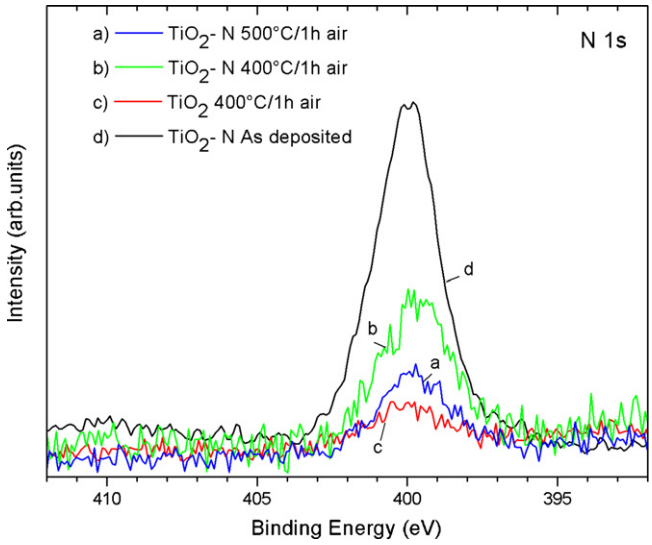

Fig. 6. XPS N 1s detailed spectra of N doped TiO_2: as deposited (d), annealed at 400 °C (b), annealed at 500 °C (a). Undoped TiO_2 annealed at 400 °C (c) for comparison.

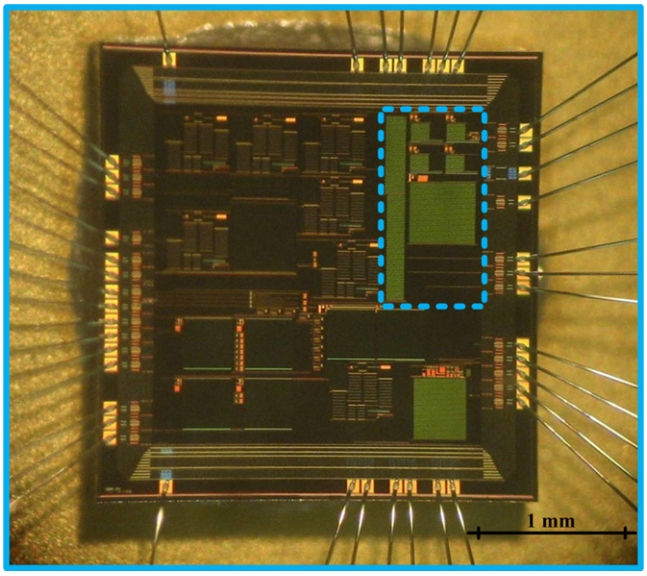

Fig. 8. Photo of the fabricated chip in 0.35 μm standard CMOS technology (the interface is in the right upper part of the figure, highlighted by the dashed line).

binding energies of Ti $2p_{3/2}$ peak located at 458.8 eV, not eventually influenced by the presence of Nitrogen atoms.

3.2. Analog integrated electronic interface for resistive gas sensors

Considering the resistive behavior of the sensor in the MΩ range, a suitable analog electronic integrated interface, whose block implementation scheme is shown in Fig. 7, has been employed [24–28]. This solution has been designed and fabricated in a standard CMOS technology (AMS 0.35 μm). These circuits, named oscillators, represent typical uncalibrated solutions for wide-range sensors which show a constant sensitivity, settable through some external parameters (e.g., resistors and/or capacitors), independent from sensor resistance value. Moreover, they offer different benefits such as, for example, an improved noise immunity and the capability to provide an output frequency (i.e., a square wave voltage signal) which can be easily post-processed in a digital manner, avoiding any ADC as next processing stages.

The integrated circuit, whose photo is depicted in Fig. 8, shows a complete chip size of $3 \times 3\,mm^2$, while the interface area is only $1.3 \times 0.65\,mm^2$, see the upper right part on the chip, highlighted by a dashed line. The small area occupied by the interface allows the circuit to be easily replied in an array configuration, so to be suitable for the development of system-on-chips (SOCs).

More in detail, referring to Fig. 8, the interface, supplied at 3.3 V, provides an output square wave voltage, whose period is proportional to the sensor resistance (named R_{SENS}) that, in this way, results to be excited through an AC signal. In particular, an integrator stage, composed by the operational amplifier OA_1 and the capacitor C, integrates the current flowing into the sensor, so performing the resistance-to-period (R–T) conversion. Each active block of the interface has been designed, at transistor level, in a standard *CMOS* technology, through a suitable operational transconductance amplifier (*OTA*), designed to show independence characteristics from temperature and supply voltage drifts, so developing a completely on-silicon integrated solution. The ideal output oscillation period T can be expressed as follows:

$$T = 4GCR_{SENS} \tag{1}$$

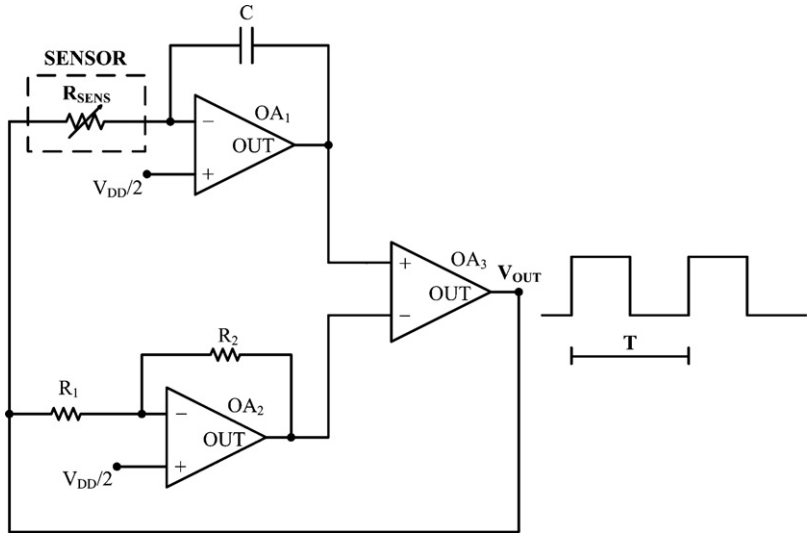

Fig. 7. Block scheme of the employed wide-range resistive sensor interface.

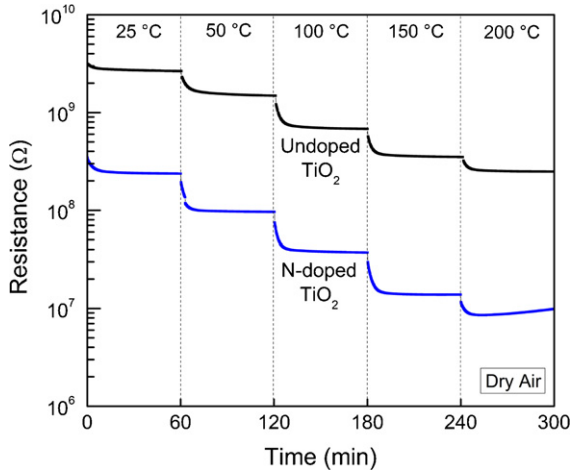

Fig. 9. Comparison of the electrical resistances of the undoped and N-doped TiO_2 sensors in dry air and operating temperatures ranging from 25 to 200 °C.

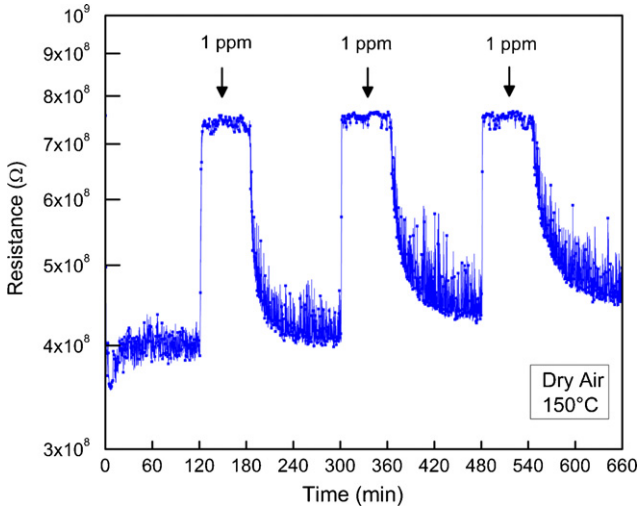

Fig. 10. Electrical response of the N-doped TiO_2 annealed at 400 °C to 1 ppm NO_2 at 150 °C operating temperature.

being G the ratio between R_2 and R_1. In this manner, circuit sensitivity has been easily set through the choice of G and C values.

3.3. Electrical response to NO_2

In order to detect the presence of gases and humidity into suitable closed chambers, experimental measurements have been conducted by means of the fabricated chip through a suitable electronic experimental apparatus composed by digital system based on a programmable logic device (PLD-based digital electronic system), with a time resolution of about 50 ns, capable to acquire and measure the output square wave period T. Experimental results have confirmed a good agreement with the theoretical expectations and calculations. In order to perform measurements of the sensor resistivity R_{SENS}, the electronic system sensitivity has been set to about 320 μs/MΩ by choosing a suitable value for the integrator capacitor (i.e., C = 100 pF).

Under dry air conditions, if the operating temperature (OT) is increased from 25 to 200 °C, the base line resistance of both the undoped and N-doped TiO_2 films decreases as reported in Fig. 9. Moreover the N-doping results to decrease the base line resistance approximately between 10 (at 25 °C) and 30 (at 200 °C) times with respect to the undoped sample. Considering that the N-doping of TiO_2 introduces acceptor states in the band gap of TiO_2 [34], the reduction of the sample resistance can be attributed to the presence of these new states, as it has been already observed [30].

Gas response characterizations have been carried out by exposing the N-doped TiO_2 nanofibers to NO_2 gas (1–10 ppm in dry air) in the temperature operating (OT) range of 100–300 °C. Optimal degassing and recovery of the base line as well as best gas sensitivity are obtained at 150 °C OT.

Considering the direct proportionality and the linear relationship between the output period T and sensors resistance R_{SENS}, as expressed in Eq. (1), and having chosen an electronic system sensitivity of about 320 μs/MΩ, the time period T of the generated square waveform ranges between 3.2 ms and 9.6 s, according to the sensor resistive values achieved through the conducted experimental measurements reported in Fig. 9.

Fig. 10 shows a typical electrical response at 150 °C OT and 1 ppm NO_2 concentration. Practical sensor sensitivity, $S = R_G/R_A$ = 1.75 at 1 ppm NO_2, have been obtained. This level of sensitivity, though measured at smaller OT, results to be much smaller than the best reported value at 300 °C OT and 500 ppb of NO_2 [15]. By exposing the film to repeated adsorption/desorption cycles high reproducibility of the electrical signal at saturation (i.e., at 1 ppm NO_2) is achieved, whereas the base line resistance tends slightly to increase with increasing signal to noise ratio. Regarding the drift of the base line one possible explanation can be ascribed to the kinetics of gas desorption, which in turns, results to be much slower than adsorption. In addition upon suppression of the "Porosity factor", which describes how the device's response (i.e., the resistance change) is attenuated in an actual porous sensing body due to a consumption of the stimulant gas during its diffusion inside [19], near field electrospinning technique enable the preparation of "pore free 1D devices" which yield response times as low as 5 and 12 s upon adsorption and desorption respectively. On the other hand the limited numbers of contacts between the fibers and electrodes increases the signal to noise ratio.

The electrical response to CO, H_2 and to 75% RH (relative humidity) has been investigated in OT range of 25–300 °C. Best operating temperatures for the detection of CO and H_2 at 250 ppm concentration in dry air were obtained at 200 °C. Fig. 11 compares the electrical response to CO, H_2 and 75% relative humidity. The N-doped TiO_2 films confirms a n-type response with decreasing resistance upon exposure to CO, H_2 and H_2O. Humidity confirms to be the most interfering gas in the whole investigated OT range. Long term stability test carried out for 6 months, revealed a substantial reproducibility of the sensor response.

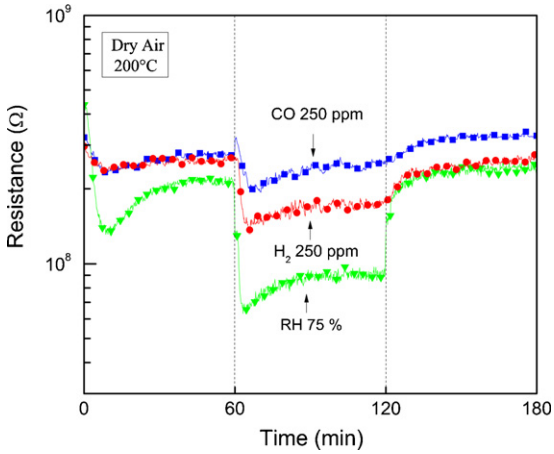

Fig. 11. Electrical response at 200 °C operating temperature of the N-doped TiO_2 annealed at 400 °C to 250 ppm CO, 250 ppm H_2 and 75% RH (relative humidity).

4. Conclusions

Controlled number of continuous well aligned crack free nanofibers 3–4 mm long and 300 μm diameter have been prepared by NFES technology. N-doping has been successfully proposed to decrease the intrinsic resistance of undoped TiO_2 fibers, whereas NO_2 measures down to 1 ppm detection limit has been performed at 150 °C operating temperature. Near field electrospinning technique enable the preparation of "1D-Pore free structures" with reduced response time in the order of seconds.

Acknowledgements

The following paper wants to be an acknowledgment to Prof. Arnaldo D'Amico, who worked with some of the authors during his teaching period at L'Aquila University (1986–1992). The sensor group at this University was born right in that period and his was the idea, advanced in that time, to join chemical, physical and electronic competencies so to have a multidisciplinary team able to design and fabricate a complete sensor system.

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Biographies

Fabrizio Ruggieri graduated in environmental science in 2001 and received his PhD in chemistry for the environment, cultural heritage and biological system in 2005 at the University of L'Aquila, Italy. He is currently a post-doctoral research at the Department of Physical and Chemical Sciences of University of L'Aquila. His work is focused on the analytical chemistry and application of nanotechnologies for environmental applications such gas sensing and water decontamination processes.

Daniela Di Camillo graduated in physics in 2010. She is a scholarship holder at the University of L'Aquila. Her work is focused on the preparation of metal oxide doped TiO_2 nanofibers deposited by near-field electrospinning for environmental applications.

Luca Lozzi received the Laurea degree in physics from L'Aquila University in 1986. In 1991 he spent 1 year at Synchrotron Radiation Center in Madison, Wisconsin (USA). Since 1991 he is assistant professor at Department of Physics, University of L'Aquila. His research activity has been focused on the electronic and structural properties of surfaces, interfaces and bulk materials (mainly oxides and organics).

Sandro Santucci graduated in physics on 1971, he is full professor in physics at University of L'Aquila and director in charge of the Physics Department. He has been director of L'Aquila Research Unit of National Institute for Physics of Matter (INFM). His key interests are development of advanced nanostructured coatings based on various physical and chemical methods and characterization of advanced coatings by various surface and bulk techniques like electron spectroscopies, electronic and scanning probe microscopies and X-ray diffractometry.

Andrea De Marcellis received the degree in electronic engineering and PhD degree in microelectronics from University of L'Aquila, Italy, in 2005 and 2009, respectively. His main research activity concerns the design of analog electronic integrated circuits, with both voltage-mode and current-mode approaches, for signal conditioning/processing and sensor interfacing in portable applications. He is coauthor of a book (ed. Springer 2011) and more than 80 scientific articles in international journals and conference proceedings. He is also co-inventor of a patent on analog system based on lock-in amplifier (2008).

Giuseppe Ferri is a professor of electronics and microelectronics at L'Aquila University, Italy. His research activity mainly concerns the design of analog electronic circuits for integrated sensor applications both in voltage and in current-mode. In this field of research he is author or coauthor of 2 patents, 2 international books and about 300 publications in international journal and conference proceedings. He is an IEEE senior member and editor of Journal of Circuits, Computers and Systems. Actually he is also the director of the Ph.D. School in Electrical and Information Engineering at University of L'Aquila.

Luca Giancaterini graduated in chemical engineering in 2010 and since 2011 he is a PhD student in materials science and engineering at the University of L'Aquila. His work is focused on the preparation of metal oxide nanocomposites thin films using physical and wet chemistry techniques for conductometric gas sensing.

Carlo Cantalini received the Laurea degree in chemical engineering from L'Aquila University, Italy, 1985. He joined in 1990, as assistant professor, the Department of Chemistry and Materials of L'Aquila University. Since the year 2000 he is associate professor of materials science. He has published numerous papers in the field of nanomaterials preparation and characterization for gas sensing applications based on metal oxide and carbon nanotubes.