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WO_3 processed by direct laser interference patterning for NO_2 detection

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ABSTRACT

In this paper two kind of sensors based on WO_3 sputtered by magnetron sputtering and annealed at 600 °C have been studied. The first kind was processed by two-dimensional direct laser interfering patterning (DLIP) and the second one without any additional treatment. Morphological and structural characterization have shown a hole structure in a periodic line-pattern for the DLIP-processed sensors and a flat surface for the only-annealed sensors, both with a tetragonal WO_3 phase. TOF-SIMS analysis has revealed that the first WO_3 layers are reduced for both samples, which could improve sensing performance. Promising response enhancement of DLIP-processed sensors has been observed for low concentrations of NO_2 (from 0.5 ppm to 5 ppm) at 200 °C, lowering the limit of detection (LOD) to 10 ppb, half of the LOD of the only-annealed sensors (20 ppb). Cross sensitivity to CO and HCHO have been investigated and the sensing mechanisms discussed.

1. Introduction

In the recent years, special attention has been paid to nanostructured materials for gas sensors, since they open a window of distinctive physical properties for a wide range of materials [1] and the physics behind is based on surface reactions [2,3]. The first chemical sensor based on nanobelts was published in 2002 by the group of Comini [4], showing a new class of stable and very sensitive nanostructured materials for gas detection. The nanostructures preparation methods can tune their structural and morphological characteristics and this allows a controlled modification of the sensor properties and performances [5–8].

Among the preparation methods, the direct laser interference patterning (DLIP) is a good candidate to modify the surface properties of metal oxide semiconductors, enhancing their sensitivity to specific gases. This technique presents some important advantages, since it combines laser heat with interference patterns able to nanostructure areas of about 1 cm^2 in less than a second. Moreover, the nanostructures can be patterned directly on the sensing device (in situ), without the need to transfer them (ex situ), as in the case of many bottom up techniques.

DLIP was successfully applied to different typologies of materials like semiconductors [9], metals [10] and polymers [11], enhancing their properties for specific applications like doped ZnO for solar cells [12,13], carbon films for tribological applications [14] and graphene oxide for humidity sensors [15].

Previous works show the good sensing capability of WO_3 towards NO_2 gas [16,17], that is one of the most harmful air pollutants as it can cause eye irritation and severe respiratory complications [18,19].

Outdoors NO_2 sources are mainly coming from automotive, chemical industry and it is also present in the acid rain, while home NO_2 sources are gas fueled heating and gas fueled stoves. Nowadays there is not a unanimous agreement on the maximum acceptable levels of NO_2 gas exposure. Nevertheless, the Environmental Protection Agency (EPA) has set 53 parts per billion (ppb) as the highest allowable limit [20] and the World Health Organization (WHO) established that 0.1 ppm of NO_2 limit indoors [19].

Therefore, monitoring very low concentration of NO_2 is crucial to keep under observation its dangerous effects and reduce the impact on the environment and human beings.

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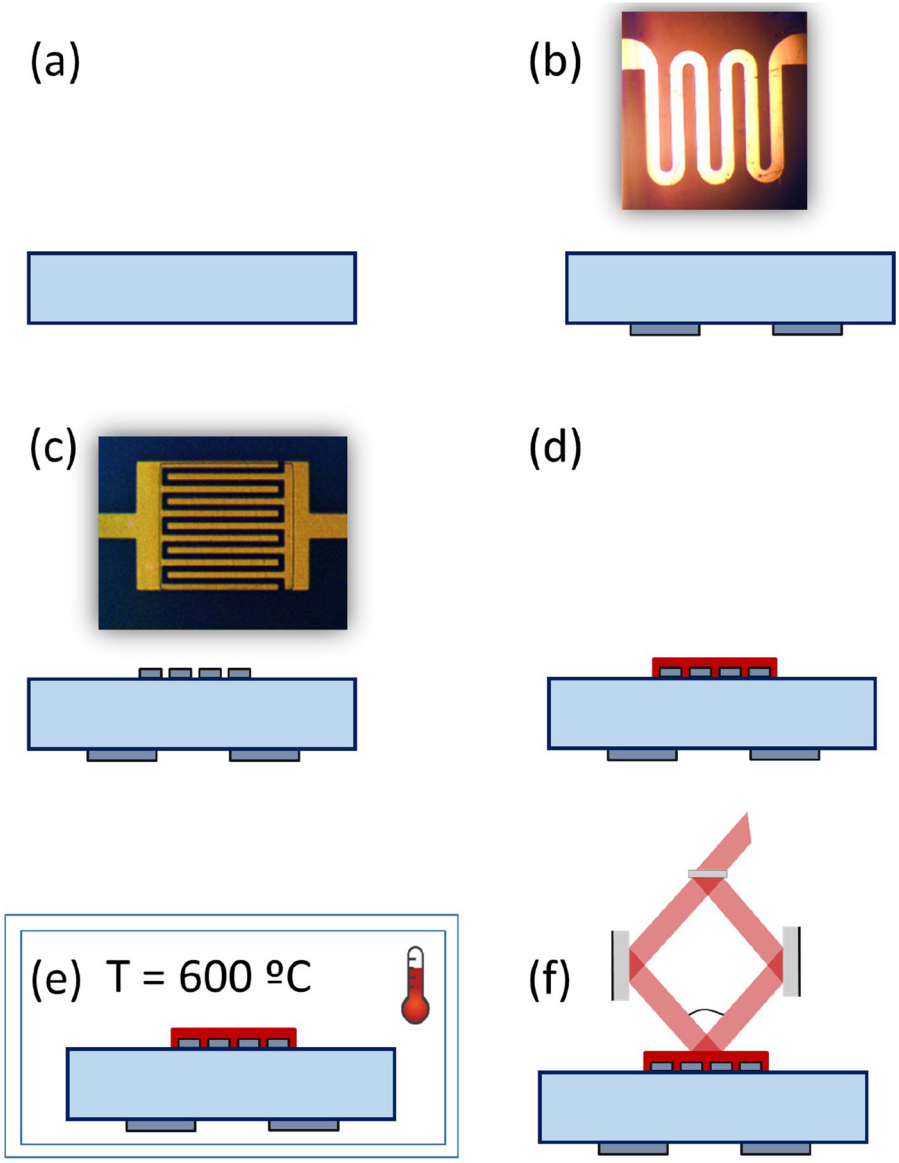

Fig. 1. Scheme of the fabrication steps of the WO_3 sensor device. (a) Polished alumina substrate, (b) DC sputtering Pt heating resistance on the reverse side, (c) DC sputtering IDT electrodes, (d) RF sputtering of WO_3 sensing layer, (e) thermal annealing at 600 °C and (f) DLIP processing at 50 mJ/cm^2.

In this work, both sensing devices, based on WO_3 thin films annealed at 600 °C and sensors annealed and processed with a two beam DLIP set up were fabricated and tested with gases. The structural properties of the thin films were characterized by surface and bulk techniques, in order to investigate the laser effect on the devices. Gas sensing performance was investigated for NO_2 detection. Conductance measurements as a function of temperature were performed in air and NO_2, in order to understand the sensing mechanism during detection process of NO_2.

2. Material and methods

2.1. Sensor fabrication

The WO_3 sensors were fabricated on $1 \times 2\,cm^2$ polished alumina substrates (Fig. 1 (a)). First of all, a Pt heating resistance was deposited on the reverse side of the alumina substrate shaped by UV photolithography and grown by DC sputtering in an Edwards ESM 100 system (Fig. 1(b)). The lift off process was carried out with acetone. The same fabrication steps were used to grow Pt interdigitated (IDT) electrodes for the electrical measurements (Fig. 1(c)). The electrodes have a separation and width of 50 µm, a length of 0.9 mm and cover an area of 1 mm^2. In order to improve the adhesion of the metal to the substrate, a 25 nm thick Cr layer was deposited under the 200 nm thick sputtered Pt layer. Afterwards, 1 mm^2 WO_3 sensing layer was deposited on top of the Pt electrodes by photolithography followed by RF reactive magnetron sputtering with a metal oxide target of 99.99% purity. The sputtering process was performed in a Pfeiffer Iontech system at 300 W of RF power in a mixed atmosphere of oxygen (40%) and argon (60%) and under 5×10^3 mbar of pressure. The sputtering time was 1 h, the deposition temperature was between 25 °C and 30 °C and as for the Pt, acetone was used for the lift off process (Fig. 1(d)). Finally, the sensor device was thermally stabilized in a quartz oven at 600 °C during 4 h in synthetic air (Fig. 1(e)). The only annealed samples were labelled TT600C. The annealing temperature was chosen considering previous results obtained by our research group [21].

After annealing, some sensors were processed by two beam DLIP set up with a frequency tripled Q switched Nd:YAG laser source provided by Thales, the Saga HP model (with a wavelength of 355 nm, a pulse duration of 8 ns, a maximum energy of 600 mJ per pulse and a

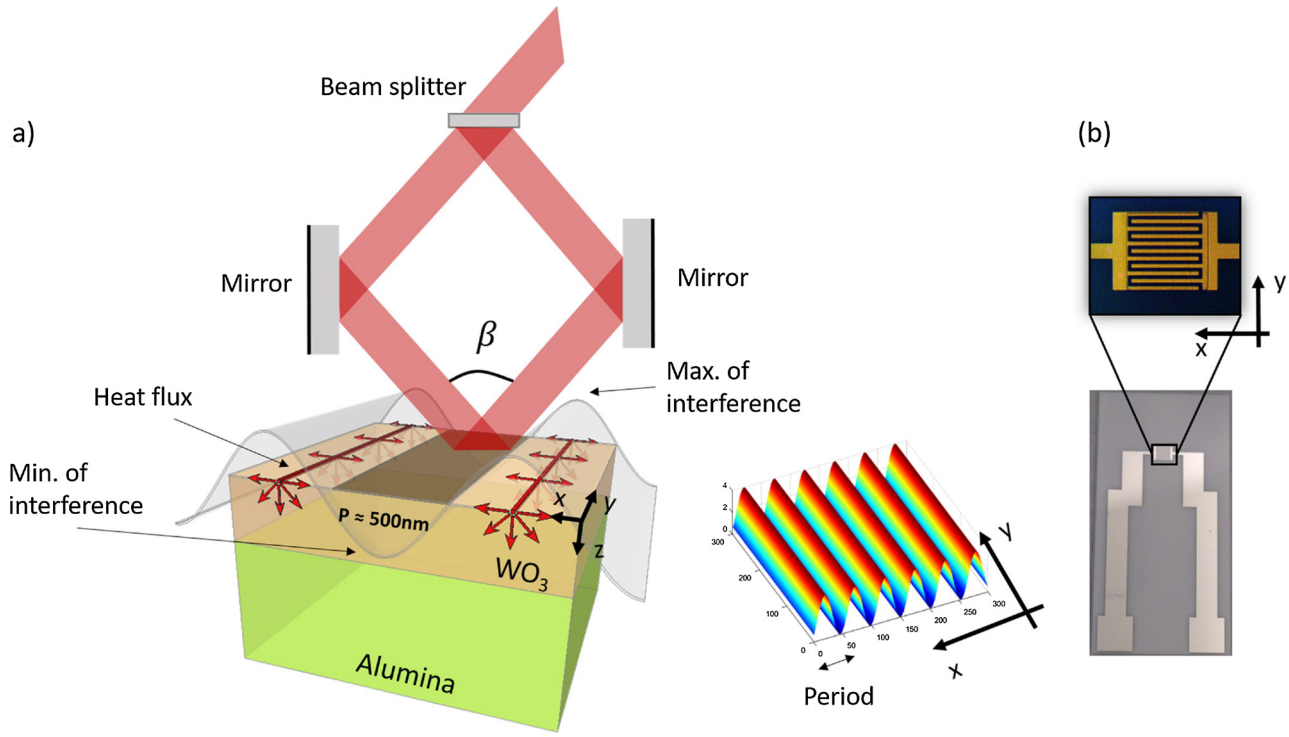

Fig. 2. (a) Schematic two-beam DLIP set-up processing WO_3 thin film on alumina and an energy distribution simulation of one-dimensional pattern. (b) Detailed image of the IDT electrodes with the coordinates, indicating that the maximum and minimum of interference are perpendicular to the electrodes.

flat top energy distribution) to obtain one dimensional interference patterns on the surface (see Fig. 1(f)). The interference patterns are a distribution of maximum and minimum intensity peaks, that lead to nanostructures down to a fraction of the laser wavelength. The areas of the material exposed to higher intensities than its ablation or annealing threshold are morphologically and structurally modified, getting melted or even removed, while areas exposed to lower intensities than these thresholds remain unaffected.

A detailed schematic drawing of the set up is shown in Fig. 2: an optical beam splitter divides the laser source into two different beams; afterwards they are reflected in mirrors and finally addressed towards the sample surface with the same incident angle. The maximum and minimum of interference are indicated with a sinusoidal wave and the heat flux generated by the laser is indicated with red arrows. An example of a typical energy distribution of two beam configuration DLIP is also shown. The maximum and minimum of interference are perpendicular to the IDT electrodes, as indicated by the coordinates in Fig. 2(b).

The period of the structure (P, distance between two maxima or two minima of interference) is defined by the angle between the two laser beams (β) and the wavelength (λ):

$$P = \frac{\lambda}{2\sin\frac{\beta}{2}} \tag{1}$$

In order to fabricate lines with a theoretical period of 500 nm, an angle of 41.5° was set up. The necessary fluence to obtain one dimensional interference patterns on the surface of WO_3 thin film annealed at 600 °C, was found to be optimum for a value of 50 mJ/cm^2 with a single shot. Samples processed at lower fluences than 50 mJ/cm^2 did not present any morphological modification. The DLIP processed samples were labelled TT600C + DLIP50.

2.2. Film characterization

For the WO_3 film characterization, samples with a size of 6 × 7 mm^2 were fabricated by sputtering and annealed at 600 °C following the same recipe as in previous section. Some samples have been also processed by DLIP, as explained in the sensor fabrication section.

The film thickness was determined by a KLA Tencor Profiler, resulting in an average thickness of 145 nm.

Regarding the morphological characterization, JPK Nanowizard 3 atomic force microscope (AFM) was employed. Tapping mode images were obtained using silicon Tap300 G cantilevers with a resonance frequency around 300 kHz. The tip radius is smaller than 10 nm and the half cone angle is around 25°.

A scanning electron microscopy (SEM) Quanta 3D FEG from FEI Company was used to study the homogeneity of the DLIP process in the sample as well as for a cross section analysis.

The X ray diffraction analysis was performed by a Bruker D8 Advance diffractometer in grazing incident (GIXRD) configuration (1.8° incident angle). The diffractometer was equipped with a copper X ray tube operating at 40 kV and 40 mA, and with a LYNXEYE XE detector. Samples were placed on a quartz zero background holder. Measuring conditions were 5 80° 2θ range, 0.02 2θ scan rate, and 0.8 s per step of counting time. The mean crystallites size, the strain of the crystallites and the cell parameters were determined by whole profile fitting Powley and Le Bail methods [22,23] as implemented in the TOPAS v 4 program by Bruker AXS [24]. The fundamental parameters approach was used for the line profile fitting [25 27]. In this approach, the instrumental component of peak broadening is calculated by the convolution of instrument profile functions for optics and X ray tube emission. Thus, the sample components to peak broadening (crystallite size and strain) are the only peak shape parameters to be optimized in the profile fitting procedure. In particular, the Double Voigt method [28] implemented in TOPAS allowed to calculate the crystallite size and strain as volume weighted for the mean column heights based on the sample dependent integral breadths of peaks.

Raman spectra were collected under ambient conditions using Horiba Jobin Yvon LabRAM HR 800 spectrometer equipped with a fiber coupled 532 nm laser. Spectra acquisition was carried out using a ×100 objective lens and 1800 g/mm grating. During the measurement, the

resulting laser power at the surface of the sample was adjusted to 4 mW. Exposure time ranged from 100 to 200 s.

The composition depth profile of different ions was measured using a time of flight secondary ion mass spectrometer (TOFSIMS 5, ION TOF). The mass spectrum was obtained by measuring the time of flight distribution of the positive ions coming from the sample surface into the detector. The primary ions source was Bi^+ operating at 25 keV and the spot size for the depth profile was 50 μm × 50 μm. Sputtering was done using 1 keV oxygen beam over a 300 μm × 300 μm of raster size area.

2.3. Electrical characterization

The response of the sensors was carried out by flowing the gases, controlled by mass flow controllers (MFC), into two cylindrical aluminium chambers of 600 and 10.8 ml.

The larger chamber was used to test the sensors at different temperatures (150 400 °C) for 5 ppm of NO_2. At the optimal temperature, lower NO_2 concentrations were tested, as well as NO_2 mixtures with CO and HCHO. The total flux into the chamber was set at 500 sccm and the uniformly gas distribution was guaranteed by a diffuser placed at the bottom of the chamber with holes disseminate at its surface.

The small chamber was used to perform the Arrhenius plots, following the steps below reported:

(i) In 400 sccm of air, the sensor was heated to 450 °C in less than 30 min and left for 10 min.
(ii) The sensor was cooled down to ~100 °C and after a minute, the temperature was increased up to ~500 °C with steps of ~5 °C/min.
(iii) The same procedure was performed in 5 ppm of NO_2.

The NO_2, CO and HCHO gases were taken from certified bottles mixed with synthetic air (Air Liquide). The circuit used to measure the sensors conductance in the presence of gas includes an inverting operational amplifier (OA) (see Fig. S1 in the Supporting Information). R_s and R_f are the sensor and the reference resistance, respectively. R_f can be freely modified and must be in the same order of magnitude as R_s. As V_{in} and R_f are known and constant, the output voltage, V_{out}, is proportional to the conductance of the sensor, G, as indicated in Eq. (2):

$$V_{\text{out}} = -\frac{R_f}{R_s} \cdot V_{\text{in}} = \text{const.} \cdot G \tag{2}$$

The output voltage is measured through a Keithley 2000 Multimeter connected via GPIB to the computer, where a Labview© is acquiring the data.

The power consumption of the Pt heating element was doubly calibrated with a thermographic camera and a Pt100 resistance, so the heater is power controlled by a voltage source. Information regarding the calibration is introduced in the Supporting Information.

In this work, the response of the devices, SR, is defined as Eq. (3):

$$\text{SR} = G_{\text{air}}/G_{\text{gas}} \tag{3}$$

where G_{air} is the conductance of the sensor in air (baseline), and G_{gas} represents the sensor conductance after 30 min of gas exposure. The recovery time is defined as the time elapsed until the 10% of the initial baseline resistance is reached after the gas extraction.

3. Characterization results

3.1. Morphological and structural characterization

The AFM image of Fig. 3(a) shows a flat surface for the sample thermal annealed WO_3 at 600 °C with a root mean square (RMS) roughness of 7 nm, while for the DLIP processed sample (Fig. 3(b) and (d)) a hole structure appears in a periodic line pattern. The RMS roughness, as the average between the processed and non processed regions, has increased to values between 10 and 15 nm. The profile section of the DLIP processed sample measured from the AFM images (Fig. 3(c)) indicates that the average depth of the holes is 18 nm. Nevertheless, from the cross section images performed by FIB (Fig. 4), the hole structure seems to be reaching the substrate, so probably the profile sections of Fig. 3(c) are underestimating the depth due to the high half cone angle of the tip.

The line patterned morphology indicates that the hole area corresponds to the places where higher intensity has been accumulated and consequently a higher temperature has been reached, melting material. Precisely, the highest area around the holes (Fig. 3(d)) seems to be the melted WO_3 moved from inside the cavities, as explained by the Marangoni convection mechanism [29].

From the SEM images (see S1 in the supporting information), a bigger area of the nanostructured sample can be analysed, showing a great homogeneity of the nanostructuring with the desired period.

Many polymorphic structures have been identified in WO_3 as a function of temperature [30 34]: monoclinic (for temperatures lower than −50 °C and from 17 °C to 330 °C), triclinic (from −50 °C to 17 °C), orthorhombic (from 330 °C to 740 °C) and tetragonal (for temperatures higher than 740 °C). Not all the transitions are reversible and the lattice constants of each crystal structure can be found in [35]. The sensing performance is expected to be affected by the crystal structure as shown by I. M. Szilàgyi et. al., who found that monoclinic WO_3 shows good selectivity to H_2S, while hexagonal WO_3 sensors present lower sensitivity but much faster response [36].

The GIXRD patterns of the as grown, only annealed (TT600C) and DLIP processed (TT600C + DLIP50) samples are reported in Fig. 5. All patterns show peaks corresponding to the alumina substrate (space group $R\bar{3}c$, PDF 010 0173). The as grown sample does not show peaks attributable to any WO_3 crystalline structure, while the only annealed and DLIP processed samples show peaks belonging to the tetragonal WO_3 structure (space group *P4/nmm*, PDF 018 1417), but the relative intensity of the (110) peak does not match the PDF data for powder tetragonal WO_3 structure, indicating that in both samples the crystallites grow with significant preferential orientation. This result is in agreement with previous investigations [21] and indicates that the laser modifications does not destabilize the tetragonal crystal structure. The stability of the crystal structure and the crystal size are important issues for the sensing mechanism [37].

Table 1 reports the cell parameters, the mean crystallites size and microstrain of the crystalline samples. Cell parameters and strain, that were calculated by Powley and Le Bail methods, are also very similar for both the samples treated and not treated with laser. Nevertheless, even if it remains within the error bars, a slight increase of the crystallite size of the DLIP processed sample compared to only annealed WO_3 has been observed.

Tetragonal phase of WO_3 is expected to appear for temperatures higher than 740 °C in bulk WO_3 [34] and the annealing performed in this work is at 600 °C. Nevertheless, in structures with nanometric crystals, as it is the case of the samples here, temperature and pressure of phase transitions can be strongly modified. A downshift in temperature for the tetragonal transition is shown in [38] for crystal sizes between 16 and 60 nm and the samples analysed here are in this range, as shown in Table 1.

Raman spectra (see Fig. 6) supports the above considerations. The as grown samples only show peaks coming from the alumina substrate [39] (highlighted with an asterisk in Fig. 6) while both samples types (only annealed and DLIP processed) present the same WO_3 Raman modes for the measured spectra.

The peaks coming from the WO_3 thin film are found at 267.7, 692.1 and 802.4 cm^{-1}. As it is known, the peaks at low frequencies (200 500 cm^{-1}) correspond to bending vibrations, while the high frequency ones that appear at frequencies between 600 and 1000 cm^{-1} are stretching modes [40]. Therefore, the lowest peak can be associated to a bending mode δ(O W O) [41] and the peaks in the range of

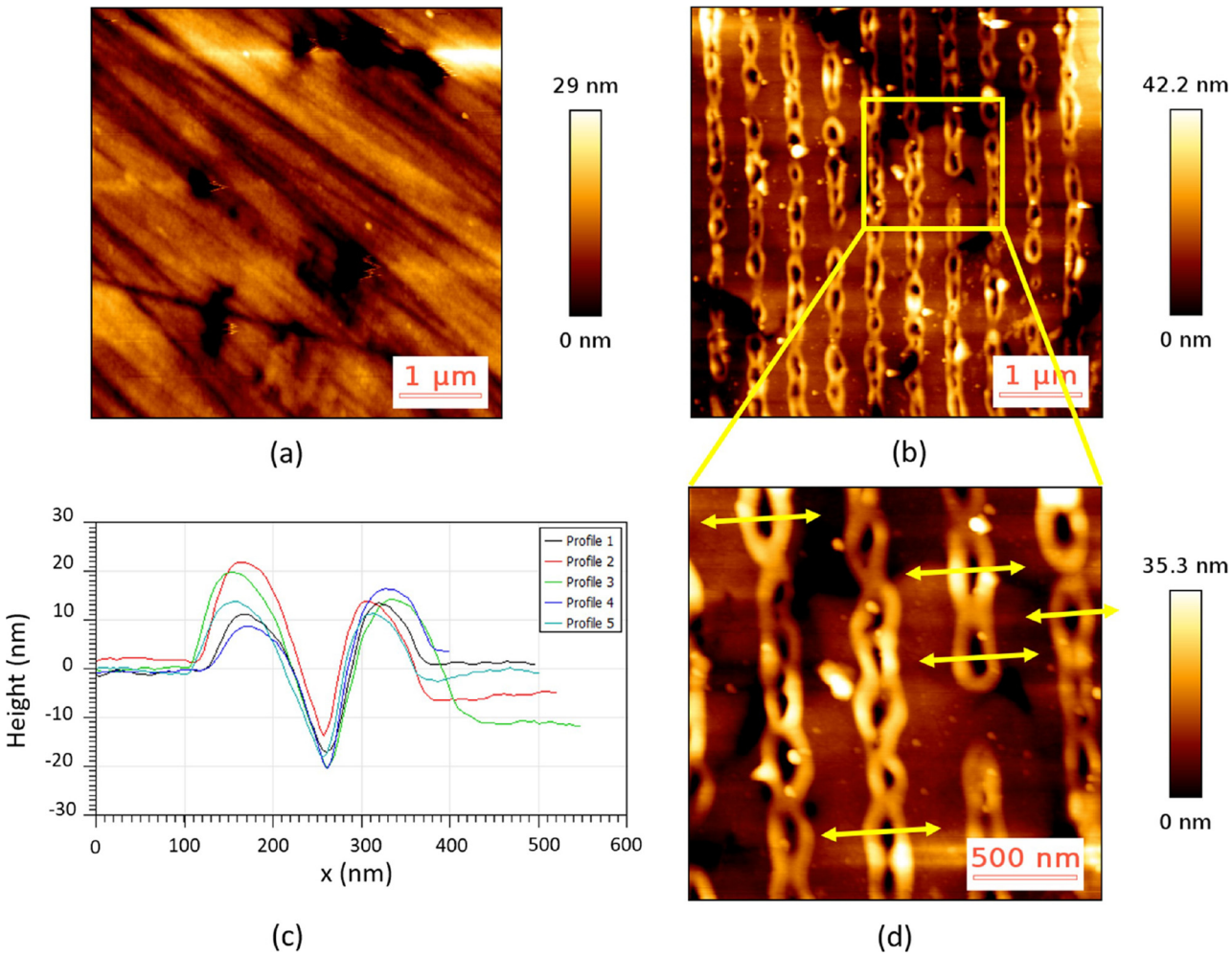

Fig. 3. AFM tapping mode images of WO_3 thin film (a) only-annealed and (b) DLIP-processed. (c) Profiles of the sections point out in (d); (d) zoomed image of the sample DLIP-processed.

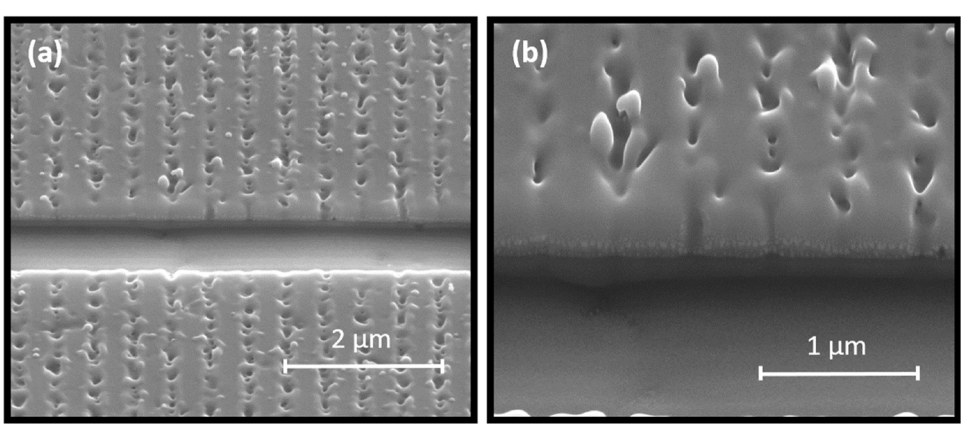

Fig. 4. (a) SEM image of a cross-section of the sample DLIP-processed and (b) a zoom SEM image of (a).

700 800 cm^{-1} are related to stretching modes O W O [42] and W^{6+} O [41], respectively.

3.2. TOF SIMS characterization

Positive TOF SIMS in depth experiments were performed to analyse the qualitative composition of the samples as a function of thickness. The detected ions related to WO_3 were W^+, WO^+ and WO_2^+ and the alumina related ions detected were Al^+ and AlO^+.

The measurements were performed twice at different sample areas with high repeatability of the results. In Fig. 7, only AlO^+ (for alumina) and W^+, WO^+ and WO_2^+ ions (for WO_3) of one of the measurements have been plotted, representing the sample behaviour. The signals shown in Fig. 7 have been filtered in order to reduce the noise gener ated by the equipment. The steepy increase in the intensity for the ion WO_2^+ in the as grown sample and the slow decrease of W^+ indicate that the sample is getting more oxidized as a function of the WO_3 sample depth. By contrast, in the other two samples, only a slight increase of

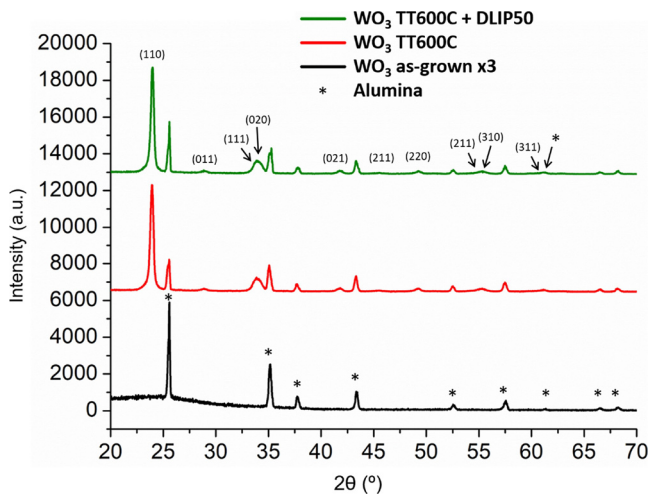

Fig. 5. GIXRD measurements of the WO_3 thin film as-grown, WO_3 only-annealed and WO_3 DLIP-processed. All patterns show peaks of the Al_2O_3 substrates marked with *, the other peaks are attributable to WO_3 tetragonal phase.

Table 1
Cell parameters, mean crystallite size and microstrain calculated by Le Bail and Powley methods for the two different samples.

Method	Parameters	WO_3 TT600C	WO_3 TT600C + DLIP50
Le Bail	a (Å)	5.2288(2)	5.2288(2)
	c (Å)	3.7963(6)	3.7974(8)
	Size (nm)	47(3)	51(5)
	Strain	0.24(1)	0.24(1)
Powley	a (Å)	5.2286(2)	5.2287(3)
	c (Å)	3.7955(7)	3.7967(9)
	Size (nm)	44(3)	49(6)
	Strain	0.23(1)	0.23(2)

the WO_2^+ and a decrease of W^+ before stabilization is shown. This result means that the first layers of the WO_3 are reduced, compared to the rest of the thin film and this could be explained by the existence of oxygen vacancies. As it is known, surface defects promote the gas detection and specially oxygen vacancies have been widely investigated as they increase the adsorption of gas molecules [43,44,7,45,46]. Moreover, the intensities of WO^+ and WO_2^+ ions are more parallel for the WO_3 DLIP processed thin film, compared to only annealed one (see Fig. 7(b) and (c)). This can be originated by a higher homogeneity degree.

The sputter rate during the TOF SIMS measurements has been calculated taking into account the WO_3 thickness deduced from cross sections observed by SEM. A small increase of the sputter rate is observed comparing the as grown with the only annealed and DLIP processed sample (see Table 2). This could be due to the increase of the homogeneity of the laser treated sample that raises the sputter velocity. The interface region between the thin film and the WO_3 is also shown in Table 2 and indicated in garnet in Fig. 7. As it is expected, the interface region increases significantly with the annealing (62.9 nm) compared to as grown (39.8 nm), because the atoms receive more energy. Therefore, a slight inter diffusion can occur at the interface between the WO_3 layer and the alumina substrate. In the case of the sample also treated by DLIP, even a larger interface region (75.2 nm) is shown. This is explained by the higher temperatures (around 1000 K) that the sample reaches with the laser shot, although the shot time is in the nanosecond scale. Similar results were found for ZnO processed by DLIP at different fluences [9].

It is well known that the diffusivity has a great role on the sensitivity and the response time as demonstrated by G. Sakai et al. [47]. The surface patterned by DLIP has clearly a higher surface to volume ratio due to the holes generated in the thin film that should improve the gas diffusion. However it remains difficult to measure such surface enhancement factor since the size of the samples is much too small to be able to carry out surface measurements by gas adsorption [48].

4. Sensor results and discussion

Due to the importance of the working temperature during the gas detection, the response to 5 ppm of NO_2 at different stationary temperatures (150 400 °C) is reported in Fig. 8. Two sensors of each type are plotted, showing a good reproducibility between sensors of the same type. At temperatures ≥250 °C, DLIP processed sensors respond to NO_2 by decreasing their conductivity but with a very low response, between 1.18 and 1.58. By contrast, sensors only annealed at 600 °C do not detect NO_2 for these temperatures or increase their conductivity (although the conductivity is increasing, the response is calculated through Eq. (3) because NO_2 is an oxidizing gas). The values of the response for only annealed sensors at temperatures ≥250 ° C range from 1.03 to 0.55.

For temperatures lower than 250 °C, the response of both sensors

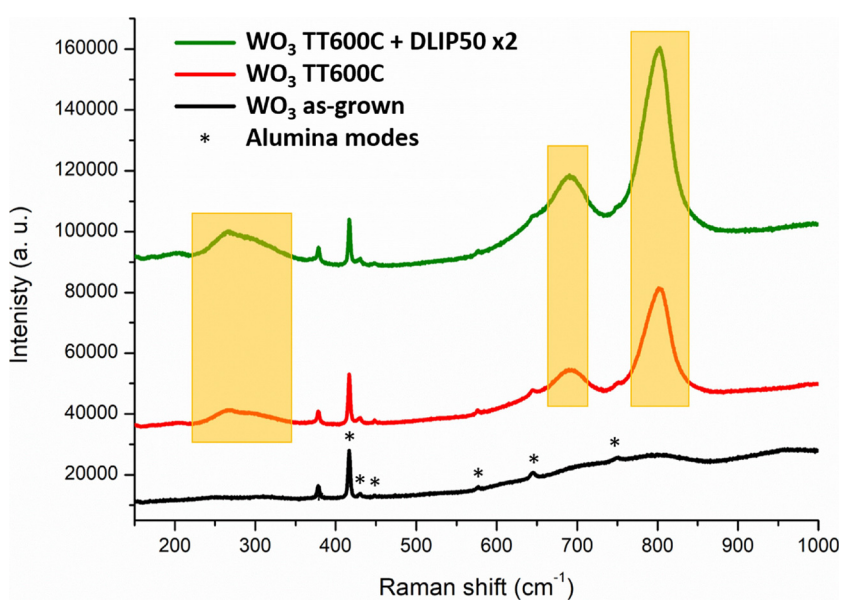

Fig. 6. Raman spectra of the WO_3 thin film as-grown, WO_3 only-annealed and WO_3 DLIP-processed.

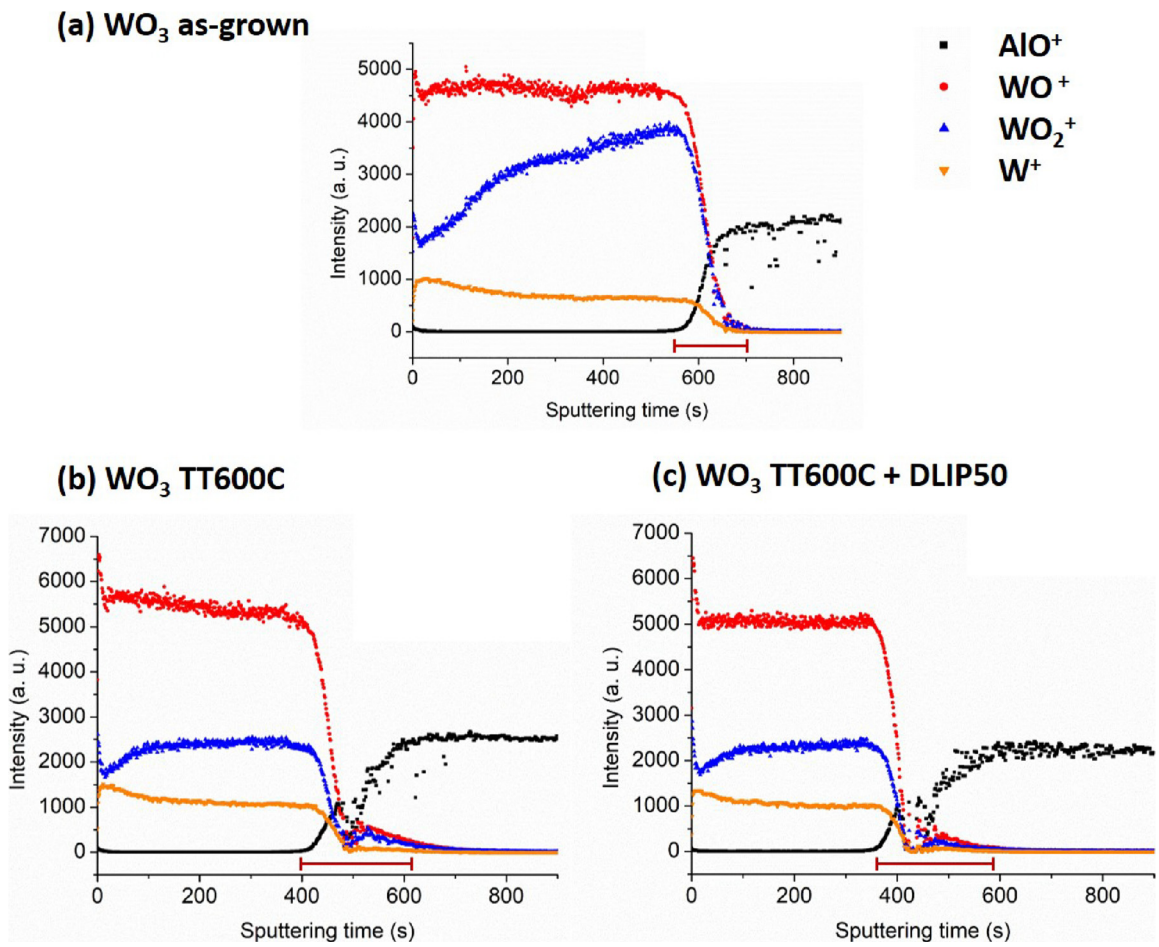

Fig. 7. TOF-SIMS measurements of AlO^+, WO^+ and WO_2^+ ions for the samples (a) WO_3 as-grown, (b) WO_3 only-annealed and (c) WO_3 DLIP-processed.

Table 2
Sputter rate during the TOF-SIMS measurements and interface region between the alumina and the thin film of the WO_3 as-grown, WO_3 only-annealed and WO_3 DLIP-processed.

Sample	Sputter rate (nm/s)	Interface region (nm)
As-grown	0.22	39.8
WO_3 TT600C	0.27	62.9
WO_3 TT600C + DLIP50	0.32	75.2

increases while decreasing the temperature, but DLIP processed sensors present responses ≃3.5 times higher than only annealed sensors. Due to the long recovery time at 150 °C (48 min for only annealed sensors and 13 min for DLIP processed sensors), the chosen optimal temperature was 200 °C for both sensors, where the recovery times were decreased to 10 and 7 min, respectively.

The sensitivity of the sensors at the optimal temperature was stu died by the response obtained at different NO_2 concentrations (Fig. 9(a)). From the sensitivity graph (see Fig. 9(b)), two different slopes can be observed for concentrations higher and lower than 2 ppm. The average sensitivity values obtained for higher concentrations are 1.74 and 0.47 ppm^{-1} for DLIP + TT600C and TT600C, respectively. Nevertheless, for the lower ones, the sensitivity values of both sensor type decrease to 0.95 and 0.20 ppm^{-1} for DLIP + TT600C and TT600C, respectively, but the reproducibility of the sensors is higher.

The limit of detection (LOD) has been calculated using the following approximation, as reported in [49]: LOD = $3\sigma/b$, where σ is the stan dard deviation of the baseline during 5 min and b is the slope of the sensitivity curve in the concentration range of 0.5 2 ppm. Nevertheless,

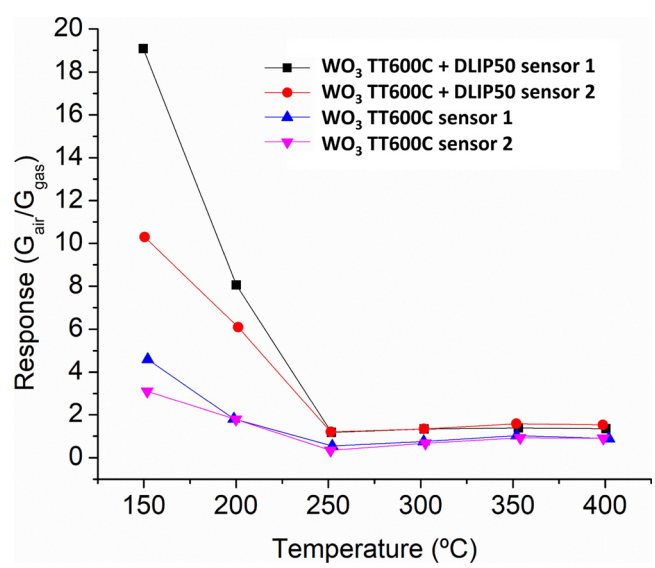

Fig. 8. Response as a function of temperature for 5 ppm of NO_2 for two sensors DLIP-processed and two sensors only-annealed.

in order to give an exact value of the LOD, measurements with ppb levels of NO_2, such as the reported in [50] should be performed. The results show that in the sensors processed by laser (LOD = 10 ppb), the LOD decreased to half of the value of only annealed samples (LOD = 20 ppb).

In order to study the cross sensitivity, mixtures of some interfering

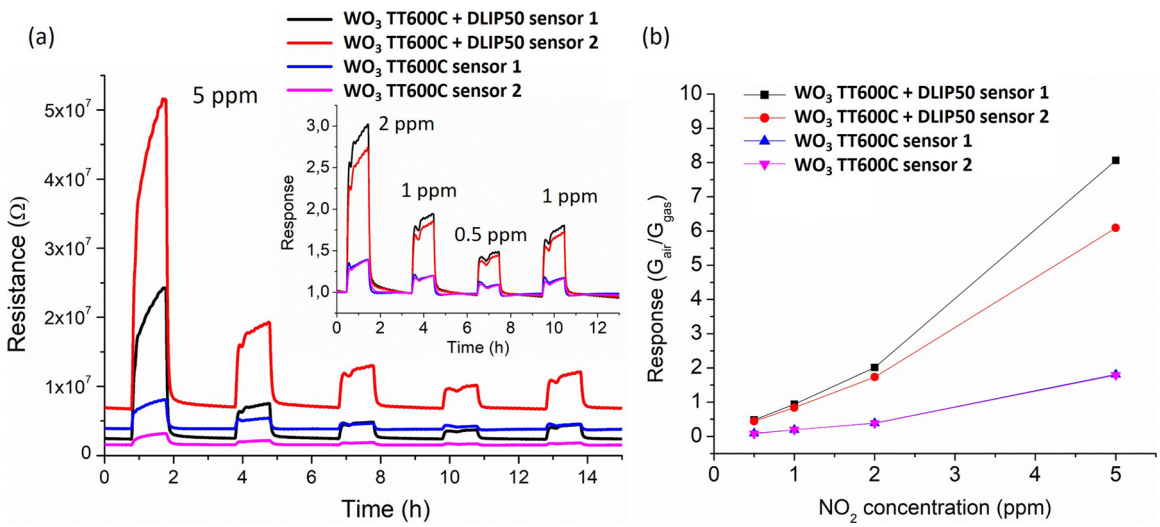

Fig. 9. (a) Resistance variation of two sensors DLIP-processed and two sensors only-annealed for 5, 2, 1, 0.5 and 1 ppm of NO_2 at 200 °C. Response of the low concentrations are shown as an inset. (b) Sensitivity of the different sensors at 200 °C for concentrations between 0.5 and 5 ppm of NO_2.

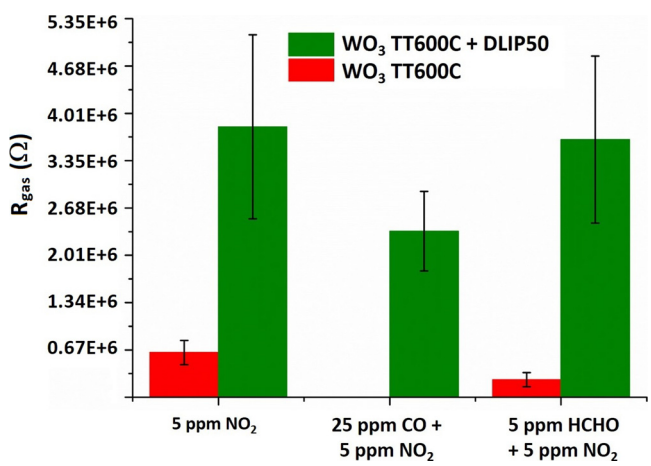

Fig. 10. Responses at 200 °C for 5 ppm of NO_2, 5 ppm of HCHO + 5 ppm of NO_2 and 25 ppm of CO + 5 ppm of NO_2.

gases with 5 ppm of NO_2 have also been tested at 200 °C, as shown in Fig. 10 (the error bars of the final resistance values have been calculated with the data of two different sensors). Common concentrations of interest for the interfering gases have been chosen: 25 ppm of CO and 5 ppm of HCHO. The results show that the NO_2 oxidizing contribution is dominant, overcoming the reducing interference, especially for the DLIP processed sensors. The performance of DLIP processed sensors makes them suitable to be employed as NO_2 sensors in atmospheres with CO and HCHO.

As shown in the previous section, significantly different responses have been found for the two type of sensors tested in the experimental conditions considered in the present work. Therefore, different detection mechanisms can be suggested in the two cases.

For low temperatures (T < 250 °C) it is generally accepted that reaction (4) takes place, where NO_2 reacts directly with the semiconductor surface, generating adsorbed NO_2 species and, consequently, decreasing the conductivity of the material [51 53].

$$NO_{2(g)} + e^- \Rightarrow NO^-_{2(ads)} \quad (4)$$

At higher temperatures, the reducing behaviour of NO_2 has also been reported for WO_3 based sensors [54], as in the current case for the only annealed sensors. It is accepted that NO_2 gas is adsorbed on the WO_3 surface forming nitrito type adsorbates (ONO^-) that after dissociate into nitrosyl type adsorbates (NO^-, NO^+). The reducing response observed for temperatures above 250 °C might be due to superior number of NO^+ adsorbates than NO^- [54].

According to the work of Yamazoe et al. [55], in the case of oxidizing gases and especially for NO_2 it had been demonstrated that a shielding effect can occur due to the oxygen contained in the background gas. In this case the power law is no more effective for very low NO_2 concentrations. The determination of the LOD by extrapolating the sensitivity curve to very low NO_2 concentration could therefore be not accurate and it would be better to make the measurements at low concentrations.

At 200 °C, the main difference between the detection mechanism of reducing and oxidizing gases is that while reducing gases interact with the adsorbed oxygen species, oxidizing agents such as NO_2 tend to be directly adsorbed on the surface (reaction (4)). On WO_3 material is difficult to absorb oxygen in an active form such as O^- and consequently the reducing agents (CO and HCHO) do not strongly modify the NO_2 response, leading to good selectivity to the oxidizing gas, specially for DLIP processed sensors.

In order to understand the oxygen species adsorbed in each type of sensor, the conductance has been measured as a function of the temperature as described in the experimental section. The Arrhenius plot in air and under 5 ppm of NO_2 are shown in Fig. 11. The method and analysis proposed by Lantto in [56] have been used to interpret the Arrhenius plot results obtained. This method relates the shape and slopes of the Arrhenius plots under different oxygen concentrations to the oxygen species adsorption. As it is also explained in [57,58], the minimum in resistance (or maximum in conductivity) at low temperatures, in the conductance variation in air, is where the O^- adsorption starts counteracting the O_2^- adsorption, as can be seen in Fig. 11. The difference between conductivity curves in air and in air with 5 ppm of NO_2 (looking at the range from 150 °C to 250 °C) is bigger for the DLIP processed sensors, which may also be related to the fact that the DLIP processed sensors present higher response to NO_2. From Fig. 11, it can be appreciated that the slopes before and after the maximum in conductance for the DLIP processed sensors are steeper than for only annealed sensors, indicating that laser treated sensors present higher concentration of sites for adsorption or physisorption. This result highlights that the DLIP processed sensors probably have laser induced defects that work as adsorption sites, apart from the oxygen vacancies revealed by TOF SIMS. This would enhance the NO_2 sensitivity, since more NO_2 molecules could be adsorbed, extracting electrons from the conduction band and thus increasing the resistance.

In fact, we consider that the conduction in tungsten oxide is mainly

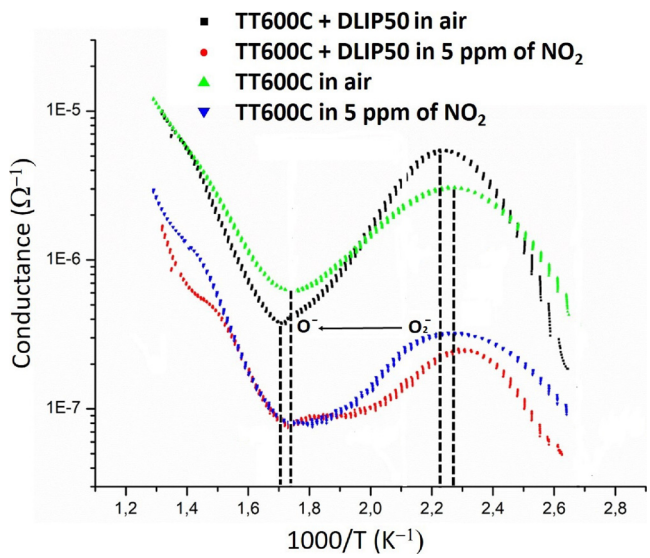

Fig. 11. Arrhenius plots in air and in 5 ppm of NO_2 for the sensors only-annealed and DLIP-processed.

due to the oxygen vacancies with a contribution of the adsorbed oxygen, as shown by the different responses to oxidizing and reducing agents. In [59], the authors study the conductivity of sputtered and thermal evaporated WO_3, whose morphology is similar to the reported in our study. In fact, the shape of the Arrhenius plot they present shows in similar experimental conditions shows correspondence to the reported in our study, with maxima and minima at similar temperatures.

5. Conclusions

One dimensional structures have been generated by DLIP technique on WO_3 thin film sensors after annealing and compared to only annealed sensors. The surface morphology modification has not affected the crystal structure, which remains tetragonal for both films, with similar crystallite sizes. Raman characterization confirms the good crystalline structure of the WO_3 and TOF SIMS analysis shows reduced layers on the top of the WO_3 film, probably due to oxygen vacancies.

Sputtered WO_3 based sensors processed by DLIP have shown responses ≃ 3.5 times higher than only annealed sensors to NO_2 at 200 °C. The LOD is 20 ppb for the only annealed sensors and it decreases to 10 ppb for the DLIP processed sensors. Besides, DLIP processed sensors show low cross sensitivity to CO and HCHO, that makes them suitable for environmental applications.

Conductance variation as a function of temperature in air atmosphere and under 5 ppm of NO_2 points out that DLIP processed sensors probably present a higher number of adsorption sites. This contributes to the enhancement of the NO_2 sensitivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.snb.2019.127226.

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