

# The role of the pulsed laser deposition of different growth atmospheres on the gas sensing properties of ZnO films

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## Abstract

ZnO films were fabricated by pulsed laser deposition using two different background atmospheres (argon/vacuum). The gas sensing properties of these materials against reducing and oxidizing gases were examined. The microstructure and crystal symmetry of the deposited films were studied with X-ray diffraction (XRD), Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman, and Photoluminescence (PL) spectroscopy. The XRD studies revealed that the ZnO films grown in an argon environment are highly textured in the c-axis with a hexagonal crystalline structure. The c-axis is perpendicular to the substrate plane orientation (002) compared to (100) plane orientation, which is developed in a vacuum environment. Usually, this orientation (100) is difficult to obtain. Raman scattering spectra for both types of ZnO films revealed the characteristic E<sub>2</sub> (high) mode that is related to the vibration of oxygen atoms in wurtzite ZnO. Moreover, PL spectra showed that a high number of defects appear in both the vacuum and argon-grown ZnO films. XPS data indicated that the O1s peak consists of several components identified as lattice oxygen, oxygen close to defects, and chemisorbed species. Furthermore, gas sensing properties were investigated for nitrogen dioxide (NO<sub>2</sub>) at different

operating temperatures and concentrations. Although both types of ZnO films have shown a good response towards NO<sub>2</sub> at ppb levels, the films prepared under vacuum conditions showed higher responses. This was attributed to differences in crystallinity, microstructure, and the type of defects present in these materials.

**Keywords:** ZnO, PLD technique, sensors, photoluminescence, surface defects, enhanced recovery, NO<sub>2</sub>

## 1. Introduction

The World Health Organization (WHO) has warned that air pollution levels are often above the maximum safe levels (threshold limit values TLV) for key pollutants as such nitrogen dioxide (NO<sub>2</sub>)<sup>1</sup>. It leads to climate change and its exposure can cause a variety of adverse health outcomes on humans, animals, and plants. The immense increase in air pollution is associated with seven million deaths yearly<sup>2</sup>. NO<sub>2</sub> exposure is linked to conditions such as heart disease and strokes<sup>3</sup>. In children, it can reduce lung growth, cause aggravated asthma, and damage buildings<sup>4</sup>. Several steps are being taken to help reduce air pollution levels across the globe. Governments are enforcing stringent pollution norms to move from coal and gas power stations and diesel generators to solar, wind, and hydropower and shift to electric cars technology<sup>5</sup>. Prioritizing walking, cycling, and public transport over cars in urban areas, deterring polluting vehicles from city and town centers is the quickest, most cost-effective way to cut nitrogen dioxide pollution levels, which are illegal in most urban areas<sup>6</sup>. The taking over of fossil fuel energy sources for renewable ones is progressive, however real-time detection and monitoring of the concentration of harmful and poisonous pollutants are required<sup>7</sup>.

Gas mixture instrumental analysis such as (GC-MS), ion mobility spectrometry (IMS), and proton-transfer-reaction mass spectrometry (PTR-MS) show significant drawbacks<sup>8</sup>. These techniques require high operational costs, complicated miniaturization, and time-consuming sample preparation and analysis. Other approaches, like electrochemical sensors, have confined temperature ranges and shorter life span<sup>9</sup>. This has motivated significant efforts for the development of sensors in the area of research to improve the levels of gas detection<sup>10</sup>. For that reason, chemoresistive sensors have emerged as a promising candidate, as they offer a more rapid,

user-friendly, miniaturized, non-destructive, and affordable detection of several toxic gases both with high sensitivity and fair selectivity<sup>11</sup>.

Chemoresistive sensors based on metal oxide (MOX) have been studied in the research area of environmental monitoring, automotive, biomedical, food quality control, etc<sup>12</sup>. These devices usually show simple measuring electronics, high sensitivity to gases, fast response, recovery dynamics, and sensor-to-sensor reproducibility<sup>12,13</sup>.

Among metal oxides ZnO is broad band gap (near 3.4 eV) semiconductor at room temperature<sup>14</sup>. Also ZnO II–VI is an n-type semiconductor with high exciton binding energy (~60 meV), non-toxicity, high surface-to-volume ratio, low cost, suitability to doping, and considerable sensitivity<sup>15,16,17</sup>. Due to these distinctive properties, it has been considered one of the most favorable materials for gas sensing, solar cells<sup>18,19</sup>, lasers<sup>20</sup>, thin film transistors<sup>21</sup>, light emitting diode<sup>22</sup>, nanophotonic and piezoelectric devices<sup>23,24</sup>. Different nanostructure of ZnO including nanorods<sup>25</sup>, nanowires<sup>26</sup>, nanoflowers<sup>27</sup> can be deposited on various substrates using variety of methodologies, such as magnetron sputtering<sup>28</sup>, thermal evaporation<sup>29</sup>, and atomic layer deposition<sup>30</sup>.

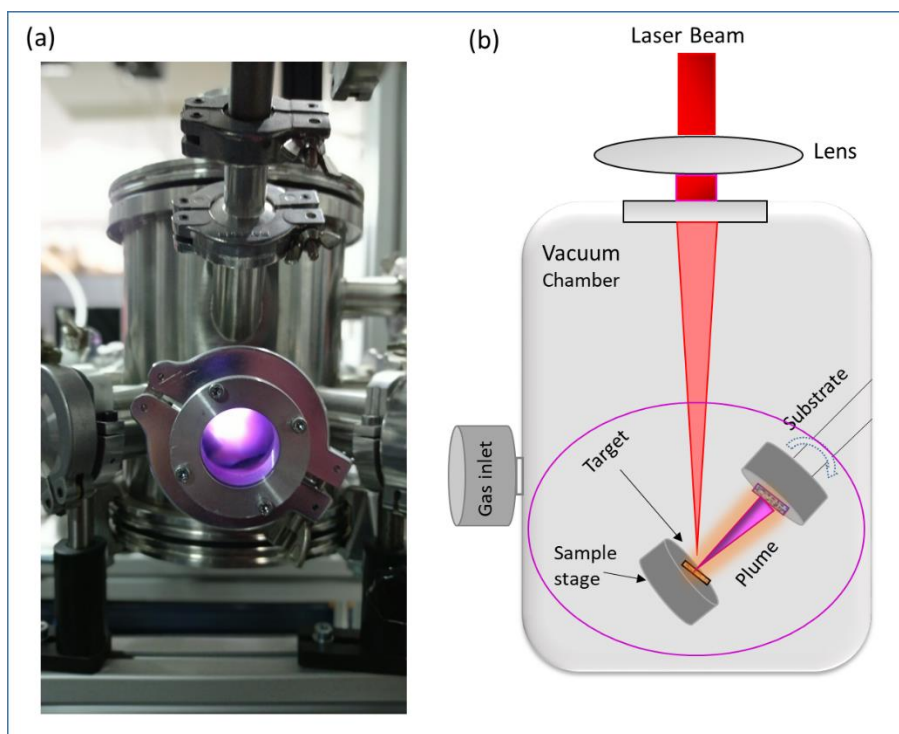
A recent report indicated that the use of gas sensing properties of pulsed laser deposition (PLD) of ZnO films are strongly dependent on the nature of the crystal surface exposed to the gas species for H<sub>2</sub><sup>31,32</sup>. The reports on EtOH and CO<sub>2</sub> sensing properties of ZnO fabricated by PLD in the air atmospheric pressure revealed the highest response attributed to adsorbed oxygen species<sup>33</sup>. Also, the photoluminescence (PL) of the PLD ZnO films annealed in the vacuum has shown in spectral features compared to argon atmosphere annealed films. It has been proposed that the broad luminescence is due to oxygen vacancies, a zinc vacancy acceptor, and a complex defect involving zinc interstitials, zinc–oxygen, anti-site defects, and oxygen vacancies<sup>34</sup>. Additionally, The detection of NO<sub>2</sub> and NH<sub>3</sub> at 10 ppm deposited onto polycor substrates under oxygen conditions was reported<sup>35</sup>. The sensing properties were attributed to the dependence of the grain size on target to substrate distance<sup>35</sup>. Despite the effort made in recent years to apply different background atmospheres to PLD ZnO films<sup>29,30,31</sup>. Most works have been examined to improve gas sensing limited to oxygen pressure or mixture of oxygen and argon background conditions of PLD ZnO films<sup>36,37,38</sup>. In addition, the available knowledge is still limited to only ZnO structure and optical quality using PLD argon-vacuum background conditions<sup>39,40,41,42</sup>.

To the best of our knowledge, the role of argon and vacuum background atmosphere (without metal catalyst) on the gas sensing properties of NO<sub>2</sub> has not been reported yet. In this regard, we propose for the first time, the successful synthesis of ZnO films by PLD (without metal catalysts) using two different background atmospheres (argon/vacuum) for the fabrication of NO<sub>2</sub> gas sensors. The structure, crystallinity, optical properties, and chemical composition of the ZnO films are characterized by FESEM, XRD, Raman, PL and X-ray photoelectron spectroscopy (XPS). Moreover, the gas sensing properties towards the detection of NO<sub>2</sub> of vacuum and argon-grown ZnO films are investigated and compared. The link between point defects, gas sensing behavior, XPS and PL results is discussed.

## **2. Experimental Section**

### **2.1. Synthesis of ZnO films**

The PLD films were obtained by laser ablation of a solid ZnO target onto silicon and alumina substrates, using the wavelength (1064 nm) of an Nd: YAG laser operating at 5 Hz with a pulse duration of 5 ns, and output energy of 340 mJ. Laser pulse energy in front of the target was 150 mJ. The Schematic view of pulsed laser deposition setup is presented in Fig.1. At a laser power density of 40 J/cm<sup>2</sup>, ZnO films were obtained after 5000 shots onto p-type Si (100) substrates, either under an Argon operating pressure of 30 Pa (>99.99% purity) or under a vacuum pressure < 10<sup>-3</sup> mbar. The distance between the target and substrate was 3 cm. The ZnO target surface was kept parallel to the substrate and inclined by 45 degrees with respect to the impinging laser pulses. Both the target holder and the substrate were kept on floating potential, at room temperature and were rotated during deposition to avoid the drilling of the target and to increase the homogeneity of the deposited films. After deposition, annealing was done for the both type of films under vacuum at 500 °C for 2h in the quartz furnace tube to obtain crystallinity.



**Fig. 1.** (a) Actual PLD setup used in this work (b) Schematic view of pulsed laser deposition setup.

## 2.2. Characterization of the Gas-Sensitive Materials.

The crystalline structure of the ZnO films was studied by XRD using the Siemens D5000 diffractometer equipped with Cu anode, Goebel mirror, and graphite monochromator in front of the point detector. The experiments were performed in the grazing incidence geometry using  $\lambda = 1.5406 \text{ \AA}$  ranging from  $20^\circ$  to  $80^\circ$  ( $2\theta$ ) with a scanning step size of  $0.020^\circ$ . Field Emission Scanning Electron Microscope (JSM-7500F) was used to examine the surface morphology of the samples. XPS measurements have been performed in a PHI 5500 Multitechnique System equipped with a monochromatic X-ray radiation source of Al  $K\alpha$  (1486.6 eV) at 350 W. The sample was placed perpendicular to the analyzer axis and calibrated using the  $3d_{5/2}$  line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The diameter circle of the analyzed area was 0.8 mm. The resolution for the general and depth profile spectra were 187.5 eV of pass energy at 0.8 eV/step, and 23.5 eV of pass energy at 0.1 eV/step, respectively. All measurements were made in an ultra-high vacuum (UHV) chamber pressure ( $5 \cdot 10^{-9}$  and  $2 \cdot 10^{-8}$  torr). The binding energies (BE) values were referred to the 1s BE at 284.8 eV. Component analysis has been performed by constructive

curve joint Shirley and Tougaard functions to determine the peak background, and the line shape of the curves was fitted with mixed Lorentzian-Gaussian at 10-30% ratio. Optical characterization was carried out by the Raman spectroscopy by a Renishaw In Via Reflex Raman spectrometer with a 442 nm excitation, and room-temperature PL measurements were made using a chopped Kimmon IK Series He-Cd laser (325 nm and 40 mW). Fluorescence was dispersed with an Oriel Corner Stone 1/8 74000 monochromator, detected using a Hamamatsu H8259-02 with a socket assembly E717-500 photomultiplier, and amplified through a Stanford Research Systems SR830 DSP. A filter in 360 nm was used to stray light. All spectra were corrected for the response function of the setups.

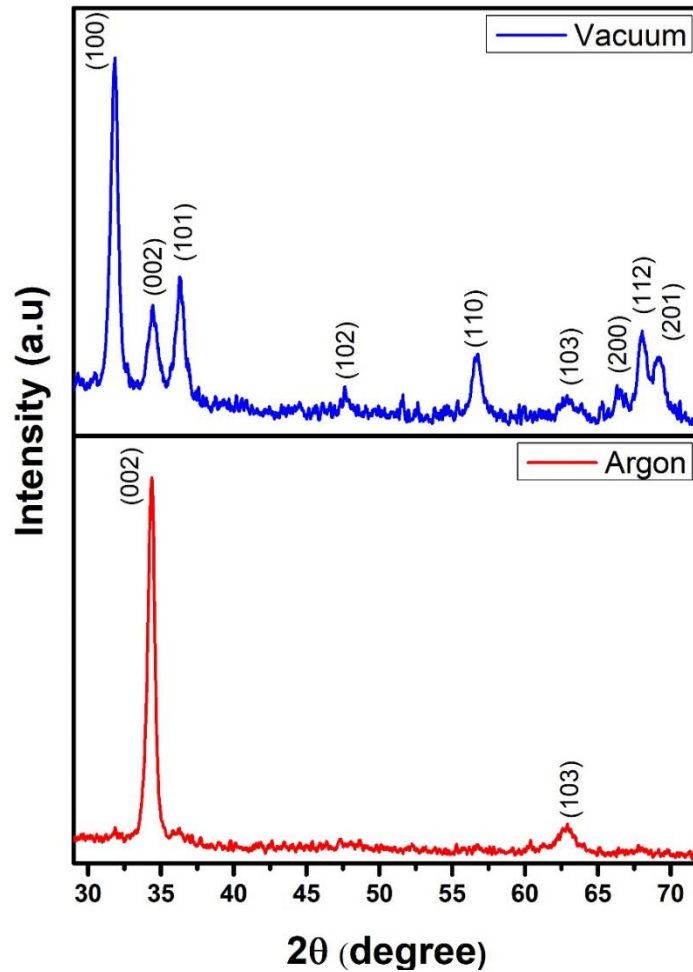
### 2.3. Device Fabrication and Gas-Sensing Measurements.

In this paper, alumina substrates (with platinum screen-printed electrodes) were coated with ZnO films by the PLD technique to achieve chemoresistive gas sensors. The response towards nitrogen dioxide at 200, 400, 600, 800, and 1000 ppb was studied. The gas sensing measurements were performed inside the 35 cm<sup>3</sup> airtight Teflon chamber. The change in the electrical resistance of ZnO films were monitored by multimeter (HP 34972A, Agilent) data acquisition system. The sensors were kept under dry air for 30 min before being exposed in repeated cycles to a given concentration of nitrogen dioxide species for 5 min. The total flow rate of gas was adjusted to 100 mL/min using a (Bronkhorst High-Tech B.V.) mass-flow gas control system that delivers reproducible concentrations of the gas tested. Gas sensing measurements were carried out in repeated cycles that consist of 30 min of exposure to a given gas concentration, followed by 30 min under dry air for cleaning and baseline recovery.

## 3. Results and discussion

### 3.1. Structural and Morphological Studies

The crystal structures and phase of the PLD grown ZnO films in vacuum and argon atmosphere were analyzed by XRD, as shown in Fig 2.

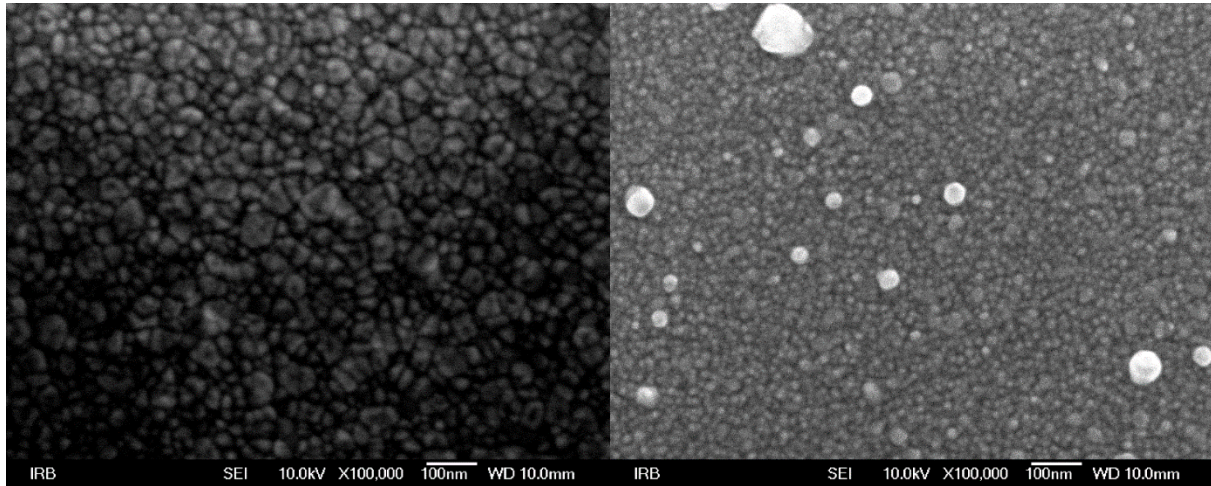


**Fig. 2.** XRD diffractograms of ZnO films fabricated by Pulse laser deposition on silicon substrate using two different background atmospheres (Argon/Vacuum).

The diffraction patterns for both types of films are indexed to the hexagonal wurtzite phase of ZnO in accordance with JCPDS card no. 00-36-1451. The strong and sharp peaks show the good crystallinity of the synthesized materials. Further, the average crystallite sizes of prepared samples were calculated using the Scherer's formula from the XRD patterns and found to be about 51 nm and 29 nm for vacuum and argon-grown ZnO films, respectively. The ZnO thin films grown by PLD in an argon environment are highly textured in the *c*-axis of the hexagonal ZnO wurtzite structure, which is aligned with the normal of the film surface. This is in line with the characteristics of the hexagonal ZnO wurtzite where the *c*-axis is perpendicular to the substrate plane<sup>43,44</sup>. In contrast, in the diffractogram associated to ZnO grown under vacuum conditions, a

significantly higher number of reflecting planes are visible indicating the polycrystalline nature of these samples.

Surface morphology studies of ZnO films have been conducted using FESEM. Fig. 3 shows the FESEM images of ZnO films at a high resolution. ZnO films grown under a vacuum atmosphere present clusters composed of multiple grains with sharp edges, suggesting a polycrystalline growth with different crystallites showing up on the surface. In ZnO films grown under argon the clusters tend to merge, forming a more compact and uniform structure composed of small grains with well-rounded shapes. Grain size of ZnO films is higher when grown in a vacuum atmosphere than when grown under argon atmosphere.



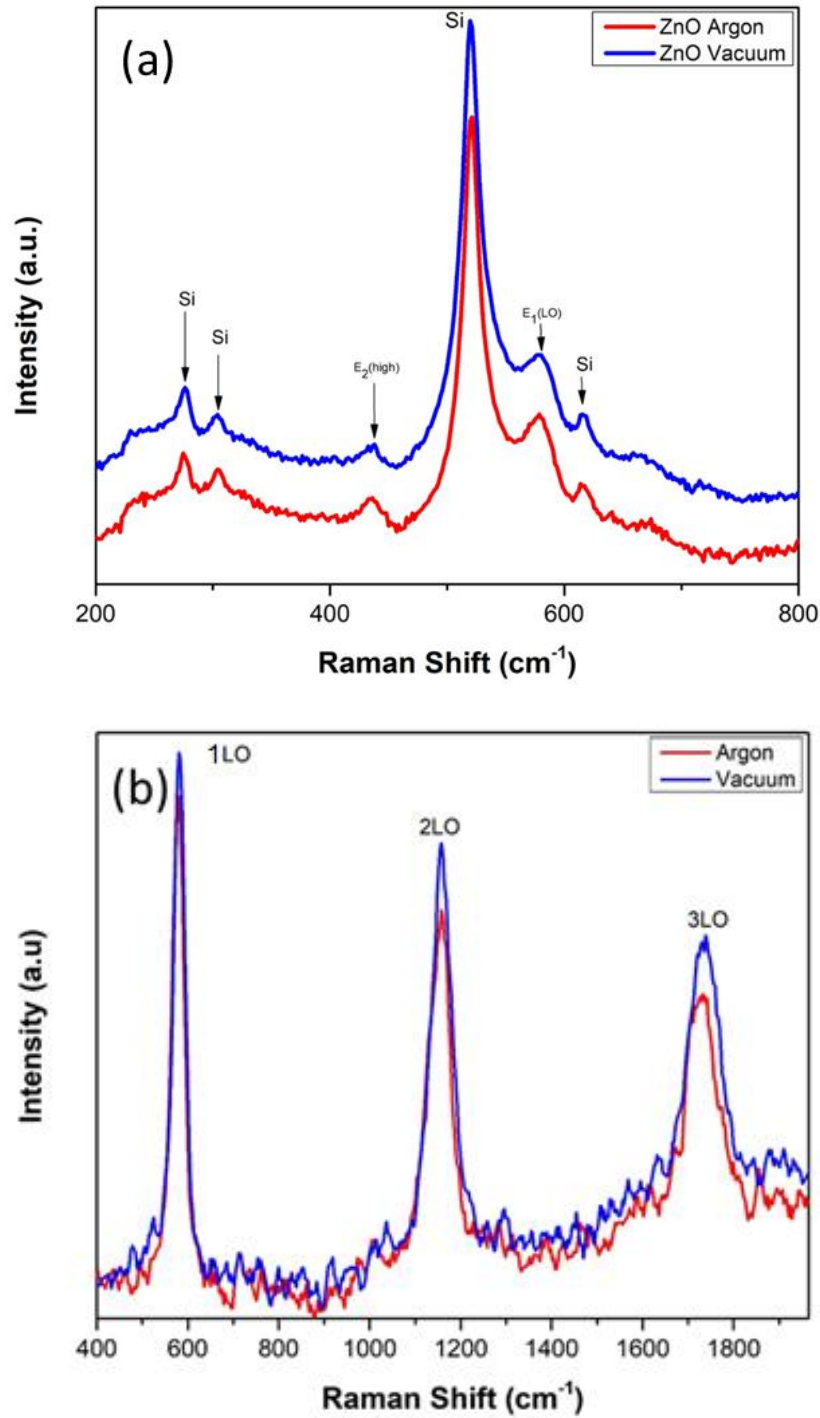
**Fig. 3.** The SEM morphology after annealing of ZnO thin films deposited in different growth atmospheres (a) vacuum and (b) argon

### 3.2. Chemical Analysis by XPS

Fig. 4 shows the results obtained by XPS analysis. The full spectra in Fig 4(a) shows the main peaks according to the expected atoms. Interestingly, just a low-intensity signal of Si is observed on both samples, which reflects a complete surface coating with the ZnO films over the Si substrates. Fig. 4(b) shows the spectra corresponding to the Zn  $2p_{3/2}$  core level, and its deconvolution in two components at around 1021.9 and 1023.8 eV corresponding to the lattice zinc (Zn-O) in the wurtzite structure and zinc interstitials ( $Zn_i$ ) or chemisorbed species,





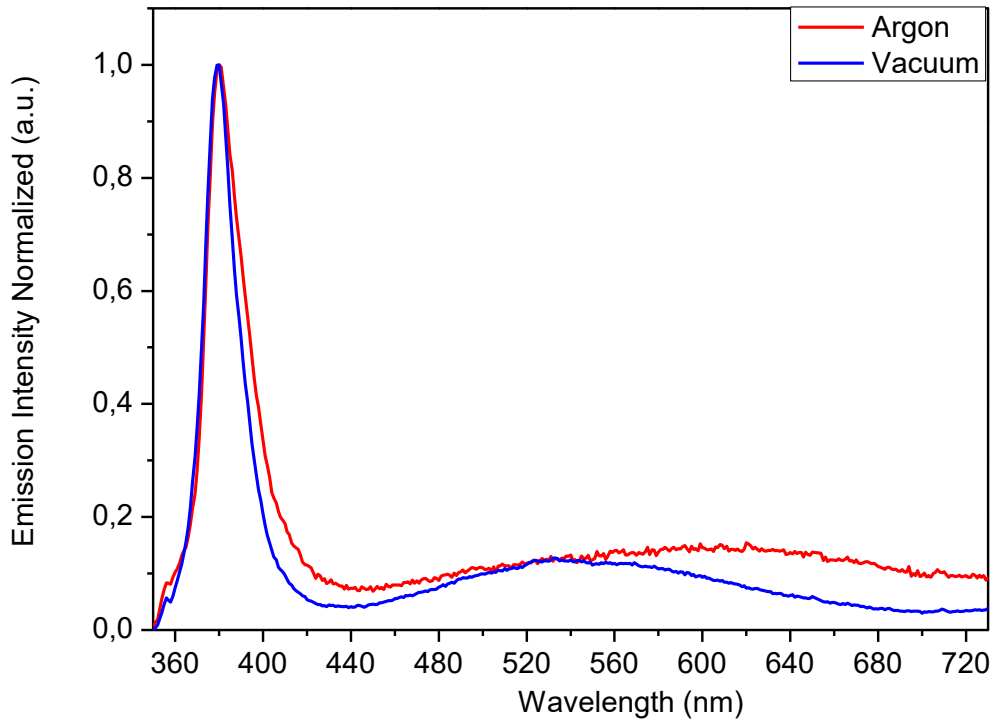


**Fig. 5.** Typical Raman spectra of the ZnO thin films (argon and vacuum) excited by laser lines at: (a) 442 nm and (b) 325 nm.

Fig. 5 (b) shows the measured resonant Raman scattering spectra of ZnO thin films argon and vacuum atmosphere, respectively. A number of longitudinal optical (LO) multiphonon peaks are

observed in both resonant Raman spectra. The frequency of the 1LO phonon peak located at  $580\text{ cm}^{-1}$  corresponds to  $E_1(\text{LO})$ , which can appear only when the  $c$ -axis of wurtzite ZnO is perpendicular to the sample surface<sup>52,53,54</sup>.

The PL spectra measured at room temperature are presented in Fig. 6. For both ZnO samples, we observed two emission bands at room temperature, a strong and narrow UV emission band centered at 380 nm originated from the direct recombination of free exciton-related near-band-edge emission (NBE) in ZnO<sup>55,56</sup>; and a weak and broad deep level emission (DLE) band in the visible range from 440 to 720 nm. The intensity of each spectrum was normalized to the intensity of the NBE emission for relative comparison. The FWHM of the NBE emission peaks are around 140 and 190 meV for the vacuum and argon samples, respectively. This broadening observed on the FWHM indicates that the quantity of intrinsic defects is higher for the argon sample<sup>57</sup>.



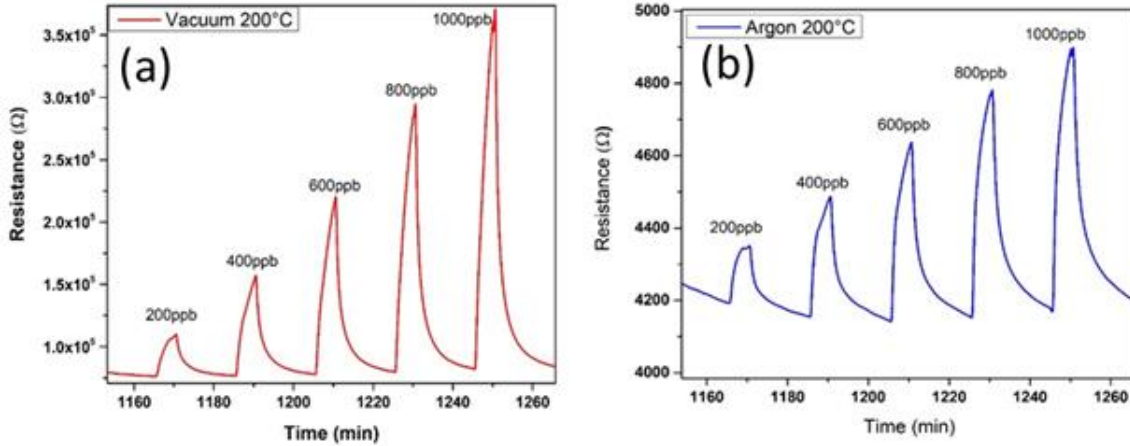
**Fig. 6.** PL spectra of ZnO films (Argon/Vacuum) at room temperature.

The broad emission band observed in the visible range is generally attributed to defects, and has the maximum emission intensity at around 520 nm “green luminescent band (GL)” and 590 nm

“yellow luminescent band (YL)” for the vacuum and argon samples, respectively<sup>58</sup>. The origin of the DLE broadband is somewhat controversial, though there have been many reports on this emission. The commonly accepted explanation is that the GL is usually believed to be associated with  $V_O$  related to structural defects, trap-states or impurity-related radiative recombination processes; and the YL band could be associated to  $O_i$ . These PL results are in agreement with the previously presented XPS results.

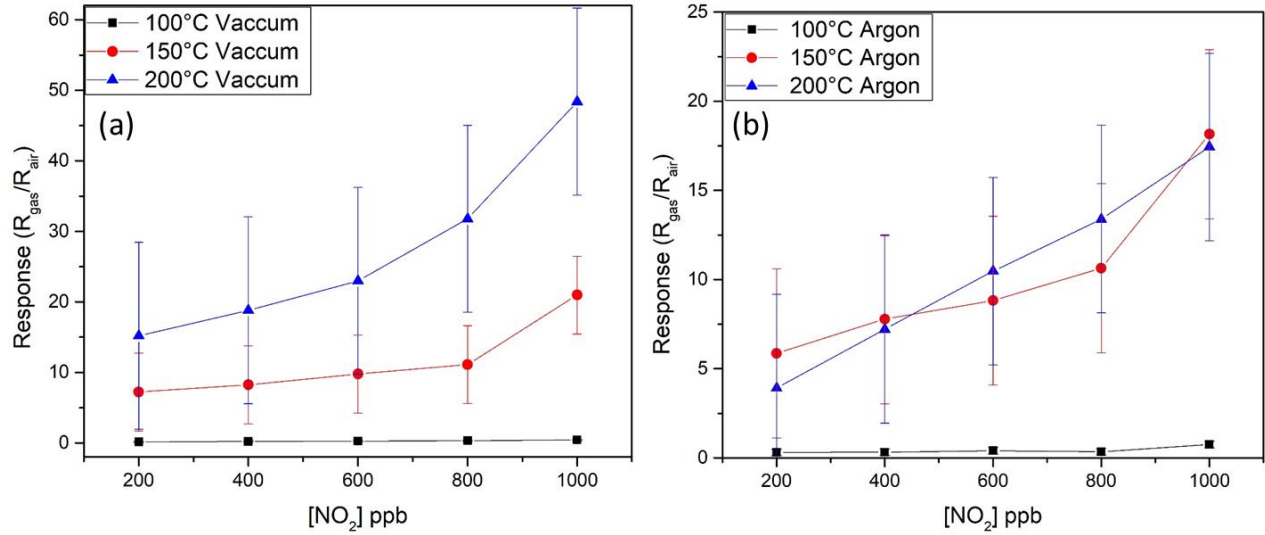
### 3.4. Gas sensing results

The gas sensing properties of the PLD ZnO films towards  $NO_2$  were studied at different operating temperatures i.e., 100, 150 and 200°C. To test repeatability, five consecutive replicate measurements and recovery sequences were performed. Fig. 7 shows the typical behavior of an n-type semiconductor exposed to repeated response and recovery cycles of increasingly concentrated oxidizing ( $NO_2$ ) species. Exposures to  $NO_2$  in an (an electron acceptor) increase sensor resistance of the n-type material. Baseline recovery is performed under pure dry air. Furthermore, during the recovery cycle, when the target gas is removed and the sensors are only exposed to dry air, they return completely to their baseline resistance, which is shown in Fig 7. The two types of sensors showed consistent and repeatable responses to various gas concentrations. The response of both films (vacuum, argon) is significantly stable because these sensors completely regain their initial baseline resistance after each cycle of measurement shown in Fig 7. The results show an increase in sensing response with each increment in analyte concentration. It has been found that recovery time was slightly longer for argon-grown films as compared to vacuum grown films. The recommended safe exposure limits to  $NO_2$  is 1 ppm which is well above the lowest concentration tested in this paper<sup>59</sup>.



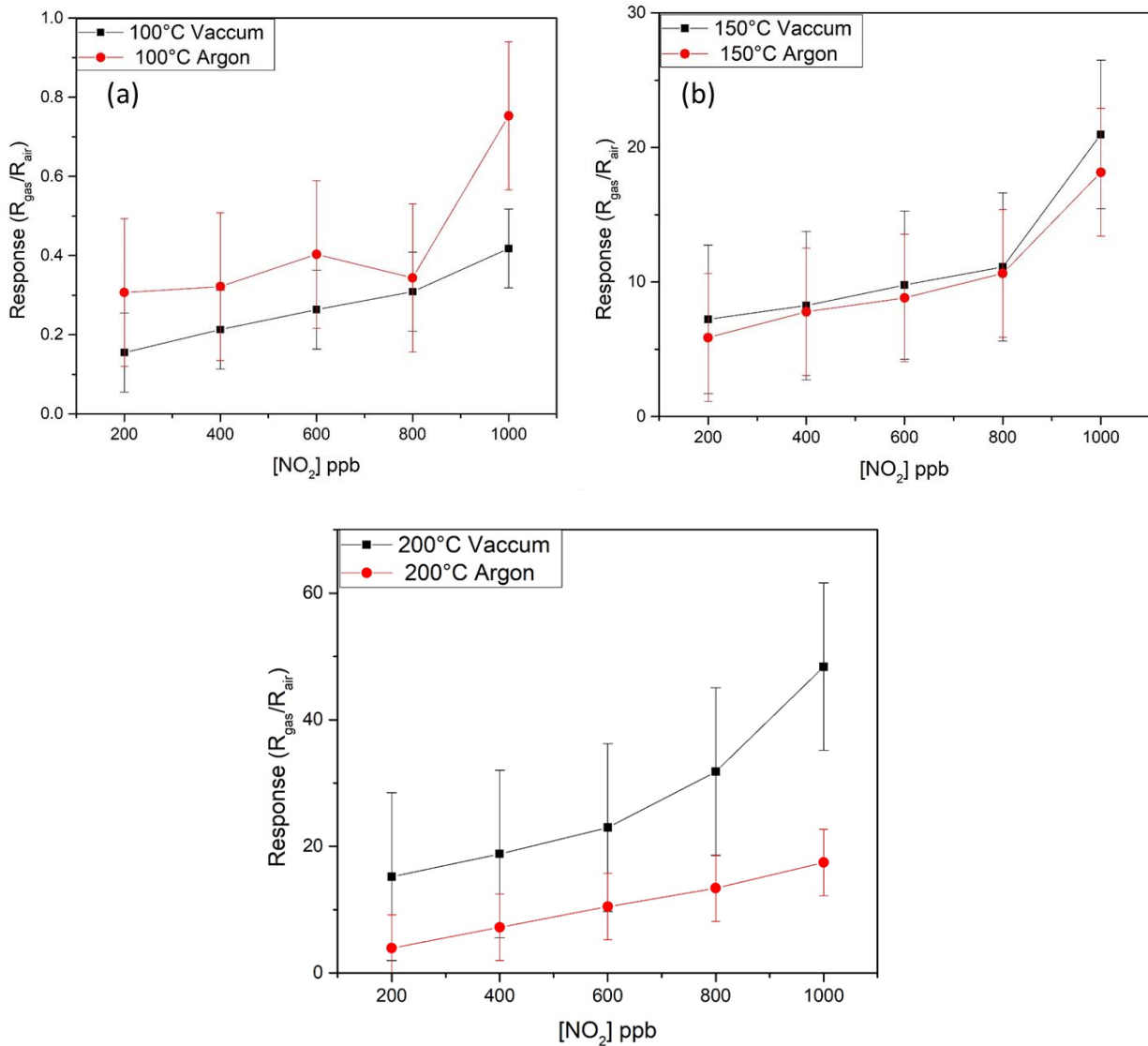
**Fig. 7.** Sensor resistance changes using the PLD ZnO films grown under vacuum (a) and argon (b) exposed to repeated exposure and recovery cycles to five increasing concentrations of NO<sub>2</sub>. Sensors are operated at their optimal working temperatures (200°C).

The (vacuum and argon) sensors were exposed to NO<sub>2</sub> at concentrations of 200, 400, 600, 800, and 1000 ppb at different working temperatures. The results are summarized in Fig. 8. When a vacuum sensor is operated at the lower temperatures tested of 100 and 150°C, it shows moderate responsiveness. When the operating temperature is raised to 200°C, a nearly 25-fold increase in NO<sub>2</sub> responsiveness is observed. The behavior of argon-grown films is very similar to the one displayed by vacuum films at 100°C. When operated at 150 and 200°C argon grown films show nearly a 10-fold enhancement in NO<sub>2</sub> responsiveness. Unlike vacuum-grown ZnO films, the responsiveness to nitrogen dioxide of argon-grown films is very similar when operated at 150 or 200°C.



**Fig. 8.** (a) NO<sub>2</sub> sensing results obtained for vacuum grown ZnO (a) and argon grown ZnO (b) at three different working temperatures.

The responsiveness for the two types of films towards NO<sub>2</sub> as a function of the operating temperature are summarized in Fig. 9. The responsiveness of vacuum or argon grown films is very similar when operated at 100 or 150°C. In contrast, vacuum-grown ZnO films clearly outperform argon-grown films when operated at 200°C. Not only the response of vacuum-grown ZnO films is about 2.5 times higher than that of argon-grown films, but also the slope of the calibration curve is higher in vacuum-grown films, indicating that these show higher sensitivity to NO<sub>2</sub>.



**Fig. 9.** Comparison of NO<sub>2</sub> sensor responsiveness for each of the 3 working temperature tested.

### 3.5. PLD Growth mechanism

In the PLD deposition process, the high-energy laser pulses interact with the target material, fixed in place by a substrate holder resulting in the evaporation of the surface layers. The evaporated material is vaporized from the target causing the formation of an expanding plasma. The plume of the ablated material gets deposited onto the substrate surface<sup>60</sup>. Plasma plumes consist of electrons, ions, atoms or molecules. After ions reach the substrate, they settle on its surface in an atomic

layer-by-layer growth process, called thin-film deposition. The different gas atmospheres and background pressures in the PLD process influence the film growth rate, stoichiometry, and crystallinity of the resulting film<sup>61</sup>. In this particular study, film growth in vacuum or in argon were implemented.

In the case of a vacuum-grown film, the plume angular distribution is formed by the collisions of the plume particles among themselves in the initial stage. The re-sputtering of ZnO from the film surface is also possible because there is no partial pressure of the gas inside chamber<sup>45</sup>. These effects favor the loss of oxygen and the growth of sub-stoichiometric oxides.

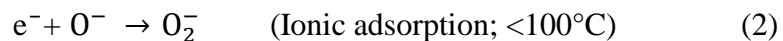
The plume expansion behavior is even more complex often in the presence of environmental gas pressure<sup>62</sup>. In the presence of an argon atmosphere, the ablated species encounter a large number of collisions with argon gas molecules, which decreases the energy of the particles reaching at the substrate and decreases the size of the ablated plume. In addition, only ZnO clusters are deposited on the substrate and Zn<sup>2+</sup> or Zn<sup>+</sup> ions are not reaching the substrate. In such a case, secondary physical processes affect the plume expansion behavior, such as plume deceleration and splitting, shock-wave formation, thermalization, etc., as a consequence of plasma-background gas interaction<sup>62</sup>.

### 3.6. Gas sensing mechanism

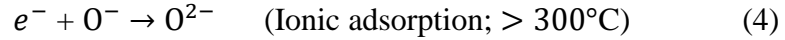
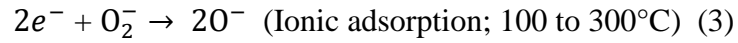
The gas-sensing mechanism in ZnO films is based mainly either by the adsorption of atmospheric oxygen on to the surface or by direct reaction of lattice oxygen or interstitial oxygen with the test gases.<sup>63</sup> The type of adsorbed oxygen species depends on temperature as described in the four steps below<sup>64</sup>.



At low temperatures, when ZnO is exposed to atmospheric oxygen, this oxygen is physically adsorbed to its surface in different molecular or atomic states without forming any ionic bond.







As the temperature increases from 100 to 150°C the dominating adsorbed oxygen species are  $O_2^-$ , when the temperature is raised from 150 up to 200°C the dominant species are atomic  $O^-$ . a further increase in the temperature would lead to the formation of  $O^{2-}$ . Physically adsorbed oxygen will capture electrons from the surface of the ZnO and form a charged oxygen surface species (steps 2-4) resulting in the development of a depletion region at the surface of the grains of the gas sensitive material. Consequently, since different working temperatures of 100, 150 and 200°C have been used, different oxygen species would be found at such temperatures as well as co-exist in the transition temperatures.

For the  $NO_2$  detection, the resistance of the ZnO sensor increases when exposed to such an oxidizing gas. The  $NO_2$  molecules reach the metal oxide surface and are directly chemisorbed on the surface of ZnO films. These oxidizing molecules take more electrons from the conduction band of ZnO and thus, the width of the depletion region is further extended, which increases the resistance of ZnO films<sup>63,71,72</sup>. According to the results presented in Fig. 8, clear differences arise between the intensity of response and sensitivity of argon and vacuum-grown films when these are operated at 200°C. When operated at 200°C, vacuum-grown films clearly outperform argon-grown films for detecting  $NO_2$ .

It has been found that gas sensitivity linearly increased with the PL intensity of  $V_O$ -related defects in both as-fabricated and defect-controlled ZnO nanowire gas sensors<sup>73</sup>. If we consider our PL analysis results, vacuum deposited films show the most intense visible emission band in their PL spectrum centered at 520 nm, which corresponds to the GL band. This means that the material with the higher number of  $V_O$  is the most sensitive to  $NO_2$ . This is further supported by the XPS analysis in which the amount of  $V_O$  is found to be higher in vacuum-grown films. Besides  $V_O$ , other factors may influence gas sensitivity. In particular, the higher polycrystallinity (revealed by XRD) and higher surface texture (as revealed by SEM) found in vacuum-grown ZnO samples may also contribute to their higher response toward  $NO_2$ .

Finally, when the gas sensors are exposed to clean air again, adsorbed NO<sub>2</sub> is released and previously trapped electrons are injected into the conduction band, reducing the width of the depletion regions at grain boundaries. This translates into a decrease in sensor resistance (the original baseline resistance is regained).

#### **4. Conclusions**

To sum up, two different kinds of ZnO films were fabricated by PLD in different background atmospheres (i.e., vacuum or argon). The gas sensing properties towards NO<sub>2</sub> have been studied. By implementing room-temperature PL studies, it has been possible to establish that the PLD background atmosphere has an impact in the number of defects and in the nature of these. PL and XPS studies indicate that vacuum-grown ZnO films show a higher number of V<sub>O</sub> than argon-grown films and this may explain the significantly higher response of the former in the detection of NO<sub>2</sub> at ppb levels, as oxygen vacancies can act as adsorption sites for the nitrogen dioxide molecule. The significant differences in the nature of defects in PLD ZnO films revealed by this study suggest that the use of different backgrounds during the growth process can be used as a suitable methodology for the engineering of defects in PLD grown nanomaterials, thus achieving functional materials with controlled properties. This approach is not only suitable for tailoring gas sensing properties but could also in photovoltaics, electronic devices or light emitting diodes.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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