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Laser annealing of transparent ZnO thin films: a route to improve electrical conductivity and oxygen sensing capabilities

Shining light to unlock functionality: we show how ultra-short-pulse laser beam scanning (LBS) transforms ZnO thin films grown by spatial atomic layer deposition (SALD). This high-throughput, low-temperature method enables scalable fabrication on large, fragile substrates, while laser annealing fine-tunes their electrical performance. By carefully optimizing pulse energy and spacing, we achieve films with drastically reduced resistivity and remarkable oxygen sensitivity. This versatile light-driven approach opens new pathways for transparent electronics and gas-sensing devices, positioning laser processing as a powerful tool for next-generation interfaces.

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# Laser annealing of transparent ZnO thin films: a route to improve electrical conductivity and oxygen sensing capabilities

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The chemical deposition of high-performance zinc oxide (ZnO) thin films is challenging, thus significant efforts have been devoted during the past decades to develop cost-effective, scalable fabrication methods in gas phase. This work demonstrates how ultra-short-pulse laser beam scanning (LBS) can be used to modulate electrical conductivity in ZnO thin films deposited on soda-lime glass by spatial atomic layer deposition (SALD), a high-throughput, low-temperature deposition technique suitable for large-area applications. By systematically optimizing laser parameters, including pulse energy and hatching distance, significant improvements in the electrical performance of 90 nm-thick ZnO films were achieved. The optimization of the laser annealing parameters – 0.21 μJ per pulse energy and a 1 μm hatching distance—yielded ZnO films with an electrical resistivity of  $(9 \pm 2) \times 10^{-2} \Omega \text{ cm}$ , 3 orders of magnitude lower than as-deposited films. This result suggests that laser post-deposition processing can play an important role in tailoring the properties of ZnO thin films. Excessive laser intensity can compromise structural integrity of the films, however, degrading their electrical transport properties. Notably, the electrical resistance of laser-annealed ZnO films exhibited high sensitivity to oxygen concentration in the surrounding atmosphere, suggesting exciting prospects for application in devices based on transparent oxygen sensors. This study thus positions ultra-short pulsed laser annealing as a versatile post-deposition method for fine-tuning the properties of ZnO thin films, enabling their use in advanced optoelectronic and gas-sensing technologies, particularly on temperature-sensitive substrates.

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## 1. Introduction

Zinc oxide (ZnO) is a versatile semiconductor material that has attracted significant interest in both fundamental research and applied science due to its exceptional physical and chemical properties.<sup>1</sup> With a wide direct bandgap of approximately 3.6 eV<sup>2</sup> and a high exciton binding energy of 60 meV,<sup>3,4</sup> ZnO exhibits promising optoelectronic and photonic performance, making it suitable for a variety of applications.

Its inherent transparency, non-toxicity, chemical stability, low cost and high durability further contribute to the potential of transparent conductive oxides (TCOs)<sup>5</sup> in applications which include gas sensing,<sup>6–9</sup> photocatalysis,<sup>10–12</sup> spintronics<sup>13</sup> and short-wavelength optoelectronic devices.<sup>14,15</sup> Additionally, ZnO is being increasingly explored in next-generation energy technologies,

including hybrid perovskite solar cells, where it plays a key role in enhancing long-term device stability and power conversion efficiency.<sup>16–18</sup> These trends underscore the growing interest in ZnO across numerous technological fields. In many of these applications, the use of flexible substrates is essential for future industrial adoption. It is thus crucial to develop growth and processing methods that operate at low temperatures, ensuring compatibility with flexible, polymer-based substrates.

Various deposition techniques have been employed to prepare ZnO thin films, including solution approaches,<sup>19</sup> magnetron sputtering,<sup>20,21</sup> chemical vapour deposition (CVD)<sup>3</sup> and pulsed laser deposition (PLD).<sup>22,23</sup> However, significant challenges still remain in coating large areas with high-quality thin films, which poses a key hurdle for industrial-scale production. Many efforts have also been made to develop cost-effective fabrication methods for ZnO thin films, but those produced through low-cost thermal processes often demonstrate limited properties.<sup>24</sup> In this context, spatial atomic layer deposition (SALD) has gathered attention due to its capability to deposit high-quality nanometre-thick materials over large surfaces with faster

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growth rates compared to conventional ALD.<sup>25,26</sup> Moreover, SALD can also be performed at atmospheric pressure, offering the same fine thickness control and high conformality typical of ALD, thus making it more suitable for scaling up to meet industrial and commercial demands.<sup>27,28</sup> As a result, SALD emerges as a highly promising deposition technique for high-quality ZnO thin films.

An effective method for improving thin film performance at low temperatures involves post-treatment of ZnO thin films.<sup>5</sup> Post-annealing processes frequently enhance the physical properties of materials, especially in TCOs.<sup>29,30</sup> High-temperature annealing can eliminate defects and promote recrystallization, thereby improving the quality and properties of the films. However, conventional resistance heating techniques often require extended operation times, consume substantial energy and are incompatible with polymeric or other soft substrates.<sup>31</sup>

Laser annealing offers a convenient solution to this problem.<sup>32,33</sup> By focusing the energy of photons on the surface of the ZnO thin film, the laser can selectively anneal the thin film while minimizing heat exposure to the surrounding areas.<sup>34</sup> With optimal laser parameters, the desired modifications can be induced in the thin film without damaging the substrate.<sup>35–41</sup> Furthermore, laser annealing can be applied over large areas with precise control over the irradiated regions, enabling patterning of selected areas under a variety of processing conditions. In addition, appropriate laser beam scanning results in recrystallization of the ZnO film,<sup>42</sup> as recently demonstrated for other functional metallic oxides.<sup>43</sup> A comprehensive study is thus convenient to assess how different laser processing parameters affect the electrical properties of ZnO and essential towards enhancing its physical and chemical properties. In particular, the use of ultraviolet (UV) wavelengths may significantly improve the electrical properties of thin films, as illumination with UV radiation has suggested that adsorbed oxygen species at grain boundaries may be neutralized,<sup>44</sup> releasing oxygen molecules<sup>5</sup> and creating oxygen vacancies within the ZnO lattice. Simultaneously, it may enhance the gas sensing response by promoting electron-hole pair generation, increasing oxygen molecule adsorption, and extracting more electrons from the conduction band compared to non-UV conditions.<sup>8,45–47</sup> This is because the 3.6 eV ZnO band gap closely matches the energy of available UV laser wavelengths (*i.e.*  $\lambda = 355$  nm).

This work proposes an innovative approach, centred on low-temperature, high-throughput growth (SALD) and UV laser post-processing annealing, to produce high-quality ZnO thin films using scalable production techniques.<sup>28,48–50</sup> The influence of relevant laser annealing parameters, in particular, laser energy per pulse and pulse overlap, on the electrical properties of 90 nm-thick ZnO films deposited on soda-lime glass substrates is studied. The temporal evolution of the electrical resistivity after laser processing in different atmospheres is also assessed. Notably, the irradiated films

show a high and reversible sensitivity to oxygen, a property we leveraged to successfully demonstrate their functionality as transparent, room-temperature oxygen sensors with a detection limit of 30 mbar constrained by our measurement set-up.

## 2. Experimental details

### 2.1. Film preparation

ZnO thin films were deposited on commercial soda-lime glass substrates with a homemade SALD system. Additional information about the SALD technique<sup>26,28</sup> and the experimental setup and process<sup>51</sup> can be also found in our previous works. Diethylzinc ((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn; DEZ, Aldrich), and water vapour were used as precursors for zinc and oxygen, respectively. The ZnO deposition process involved 600 cycles for estimated film thickness of *ca.*  $90 \pm 5$  nm, based on the growth per cycle (GPC) of the process used at 65 °C, while the precursors were kept at room temperature. The substrate oscillated under the injector at a distance of 150  $\mu$ m with a speed of 10 cm s<sup>-1</sup>. The film thickness was also estimated using a FS-1 multi-wavelength compact ellipsometer (Film Sense). The obtained films were cut in  $1 \times 1$  cm<sup>2</sup> squares (*W*) for this study.

### 2.2. Post-deposition treatment

The annealing processes applied to the SALD deposited samples were performed using an ultraviolet pulsed laser (Rofin-Sinar, Germany) with an emission wavelength  $\lambda = 355$  nm, and a pulse duration  $\tau = 300$  ps. The laser provides a maximum output power of 2.3 W with a linearly polarized beam output. The beam exhibits an elliptical Gaussian profile with 1/e<sup>2</sup> intensity decay dimensions<sup>52</sup> of  $2a = 34$   $\mu$ m and  $b/a = 0.86$  at the working distance.

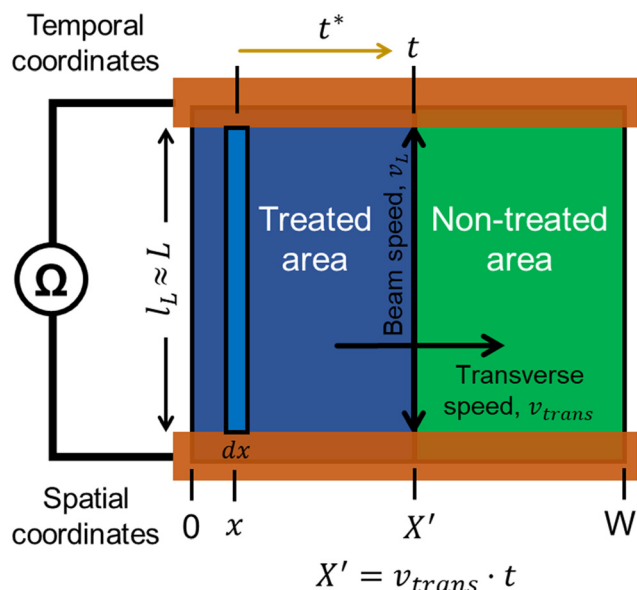
The laser is equipped with galvanometric mirrors so that the spot can define a 1-dimensional scan of length  $l_L$  along the surface of the sample at different beam speeds,  $v_L$ . Unless otherwise indicated, a speed  $v_L = 800$  mm s<sup>-1</sup>, and a pulse repetition frequency  $f_{rep} = 800$  kHz, were applied in this work (*i.e.* the distance between two consecutive pulses in one line was 1  $\mu$ m). In order to scan a 2-dimensional (2D) region, the system allows to define the distance between consecutive beam scanning lines, *i.e.* the hatching distance,  $\delta$ . Laser processing was performed in beam scanning mode, without moving the sample. Laser pulse energy,  $E_p$ , as well as pulse and line-to-line overlap were varied in order to improve the properties of the resulting films.

Unless otherwise indicated, the samples were processed in an evacuated chamber at pressures of 30–38 mbar using a rotary pump. Additional experiments were performed with the films under air, nitrogen and argon pressures.

Transmittance measurements were carried out using a PerkinElmer Lambda 750 UV-vis/NIR spectrophotometer equipped with an integrating sphere.







**Fig. 1** Scheme of the UV laser beam scan process applied to anneal ZnO thin films, during *operando* measurement of their resistance with 2-points. The laser beam scans a line of length  $l_L$  and the equivalent transverse velocity of the laser front, as explained in the text, is defined by  $v_{trans}$ . The voltage taps (orange rectangles) are separated a distance  $L$  ( $\approx l_L$ , length of the 1-D scan).  $W$  is the film width.

### 2.3. Film characterization

Thin film electrical resistance ( $R$ ) was measured with a Keithley 2000 multimeter connected to a 4-point probe station. In the case of the laser *operando* measurements, a 2-point method was used, as shown schematically in Fig. 1. In the latter measurement configuration, two homemade electrodes (2 mm-wide copper strips) were carefully positioned to rest fully on the film, each covering an entire side of the sample. The distance between both voltage taps was fixed at  $L \approx 4.5$  mm. The resistance of the electrodes in short-circuit was determined as  $< 2 \Omega$ , which is negligible compared to the resistance of the film. Unless otherwise indicated, the electrical measurements were performed at room temperature in ambient atmosphere.

The surface microstructure was characterised using a FEG ZEISS Gemini 300 field-emission scanning electron microscope (SEM, Carl Zeiss, Jena, Germany) operated at 10 kV.

The structural characterization of the ZnO thin films was carried out using X-ray diffraction (XRD) in Bragg-Brentano geometry using a PANalytical Empyrean system, equipped with a copper anode X-ray source ( $\lambda = 1.5418 \text{ \AA}$ ) and a PIXcel linear detector covering an angular range of  $3.3^\circ$ , and a step size of  $0.013^\circ$  and a time per step of 300 s. X-ray photoelectron spectroscopy (XPS) measurements were performed in selected samples with a Kratos Axis Supra apparatus using Al  $K_\alpha$  radiation (1486.6 eV). The lateral size of the region explored was  $0.7 \times 0.3 \text{ mm}^2$ . The spectra were charge-corrected to the main line of the carbon 1s spectrum (adventitious carbon) set to 284.8 eV.

A calibrated Nexis GC-2030 gas chromatograph was used to determine the composition of the treatment and measuring atmospheres. Argon and oxygen could not be separately quantified with the available gas column.

## 3. Modelling of the laser annealing process

Laser processing can be studied so as to assess the induced phenomena occurring during *operando* measurements. A schematic representation of the beam scanning mode and the *operando* measurement set-up is illustrated in Fig. 1.

The 2D laser scanning process performed in this experiment is closely related to the hatching distance ( $\delta$ ), in turn determining an equivalent transverse velocity of the laser front,  $v_{trans}$ . This velocity is related to the length of a one-dimensional scan ( $l_L$ ) and the beam speed ( $v_L$ ) through the relationship presented in eqn (1).

$$\frac{l_L}{v_L} = \frac{\delta}{v_{trans}} \quad (1)$$

The temporal evolution of the complete sample resistance, while the laser is irradiating the film, can be evaluated considering the following. Once the laser irradiates a given area of the sample, the resistance of such area is suddenly lowered during a short initial stage, and it is followed by a slow increase thereafter. With this assumption and considering the measurement set-up, the sample resistance is evaluated as the contribution of two resistances in parallel that vary with time: the first one associated to the untreated region ( $R_{untreated}$ ), and the second one to the laser-treated region ( $R_{treated}$ ), as illustrated in eqn (2).

$$\frac{1}{R(t)} = \frac{1}{R_{untreated}(t)} + \frac{1}{R_{treated}(t)} \quad (2)$$

The resistivity of the untreated region ( $\rho_0$ ) is considered to be that of the as-deposited ZnO film. For the calculation of the resistivity of the laser-treated regions ( $\rho_1$ ), the sample was divided into differential regions of width  $dx$  that were processed in a given time. As mentioned earlier, each of these regions exhibits a strong initial reduction of the resistivity due to the laser irradiation and evolves with time from the end of the laser treatment until the measurement takes place. By defining  $t^*$  as the time between the instant when the laser irradiates a certain  $dx$  region and the measuring time ( $t$ , see Fig. 1), the following equation can be written (eqn (3)):

$$t^* = t - \frac{x}{v_{trans}}, \quad (3)$$

The resistivity  $\rho_1(t^*)$  would be obtained from eqn (4).

$$\rho_1(t^*) = \beta(t^*)\rho_0 = \beta_0 f_1(t^*)\rho_0 \text{ with } \beta_0 < 1 \quad (4)$$

where  $\beta(t^*)$  is the function that models the time evolution of each  $dx$  portion of the film during and after the laser



irradiation.  $\beta_0$  accounts for the initial resistivity reduction and  $f_1(t^*)$  considers the time evolution of the resistance after the laser irradiation. Therefore, the time evolution of the resistance of the laser treated area can be evaluated by eqn (5).

$$\frac{1}{R_{\text{treated}}(t)} = \int_0^{X'} \frac{e}{\beta_0 \rho_0 L f_1(t^*)} dx, \quad (5)$$

where  $X'$  is the position of the laser scanning line at time,  $t$ ,  $e$  is the film thickness, and  $L$  the distance between contacts. On the other hand, the resistance of the untreated region can be directly calculated using the following relation (eqn (6)):

$$\frac{1}{R_{\text{untreated}}(t)} = \frac{(W - v_{\text{trans}} \cdot t) \cdot e}{\rho_0 \cdot L} \quad (6)$$

where  $W$  refers to the total width of the film.

## 4. Results and discussion

### 4.1. Evolution of the electrical properties of ZnO films with varying laser processing parameters

Fig. 2 illustrates the evolution of the electrical response of a SALD ZnO thin film as a function of energy per pulse for different hatching distances. The remaining laser processing parameters are outlined in the experimental section. The high optical transparency of ZnO is confirmed to be preserved after laser annealing of the thin film, as shown in Fig. S1 in the SI. The transmittance of laser treated samples is indeed equivalent to as-deposited samples using the same SALD process.<sup>53</sup>

As deduced from Fig. 2, large variations of the electrical resistance of the ZnO films can be achieved by controlling the laser annealing. More specifically, the initial insulating behaviour of the as-deposited ZnO films is modified as the

pulse energy increases, leading to reduced sheet resistance values. For optimum processing conditions ( $E_p = 0.21 \mu\text{J}$  and  $\delta = 1 \mu\text{m}$ ) the resistance decreases down to 115 k $\Omega$ . Considering the measurement set-up, the lowest electrical resistivity values  $\rho = (9 \pm 2) \times 10^{-2} \Omega \text{ cm}$  for the laser annealed ZnO thin films correspond to electrical conductivity values of  $11 \pm 6 \text{ S cm}^{-1}$  and a sheet resistance value of  $(1.0 \pm 0.2) \times 10^4 \Omega \text{ sq}^{-1}$  under optimum conditions for the 90 nm ZnO films.

As deduced from Fig. 2, the laser parameters exert a strong influence on the resistance values of the films, although a critical optimum condition may not be identified, *i.e.* there is a range of pulse energies and hatching distances which yield improved electrical properties for these films. Thus, for  $\delta = 2 \mu\text{m}$  and  $4 \mu\text{m}$ , this window ranges from 0.1 to 0.4  $\mu\text{J}$  per pulse, while the range becomes broader for  $\delta = 1 \mu\text{m}$ , extending from 0.1 to 0.6  $\mu\text{J}$  per pulse. It is thus clear that both, pulse energy and the spacing between consecutive laser lines, significantly influence the evolution of the electrical properties. Hatching determines the 2D pulse overlap, which in turn governs various physical processes during laser annealing. The best performance observed for the smallest hatching distance can be attributed to increased heat accumulation during laser processing upon reducing  $\delta$ , also enhanced by a pulse duration in the hundreds of picoseconds. At the same pulse energy, a shorter hatching distance results in greater heat accumulation and prolonged high-temperature exposure, leading to slower cooling rates. This effect helps preserve the integrity of the film, thereby extending the range of pulse energies that yield enhanced electrical properties.

Fig. 3 shows SEM images of the ZnO film surface as-deposited and after UV laser irradiation with  $\delta = 1 \mu\text{m}$  and different pulse energy values. A comparison of Fig. 3(a) and (b) confirms that the low laser energy treatment (0.21  $\mu\text{J}$ ) that provided the best electrical results preserves the integrity of the film. In contrast, pulse energies exceeding the optimal range mentioned above result in significant changes in the films. Consequently, the progressive formation of domains on the sample surface, which reduce percolation between ZnO islands (Fig. 3(c)), can explain the increase of resistance observed for this condition. The surface topography resulting from higher pulse energies (Fig. 3(d)) suggests the occurrence of melting and recrystallization processes. A large molten volume triggers an increased influence of surface tension in relation with the film-substrate interaction forces. These phenomena enhance the formation of melt droplets and a consequent progressive separation of ZnO domains, which result in the ultimate formation of separate ZnO islands, in agreement with the electrical insulating behaviour observed in Fig. 2 for this condition.

The proposed picosecond laser annealing induces significant modifications in the crystallinity of the ZnO thin films, as shown in Fig. 4. With low pulse energies ( $<0.38 \mu\text{J}$ ), no substantial changes are observed in the crystalline structure. At higher pulse energies, however,

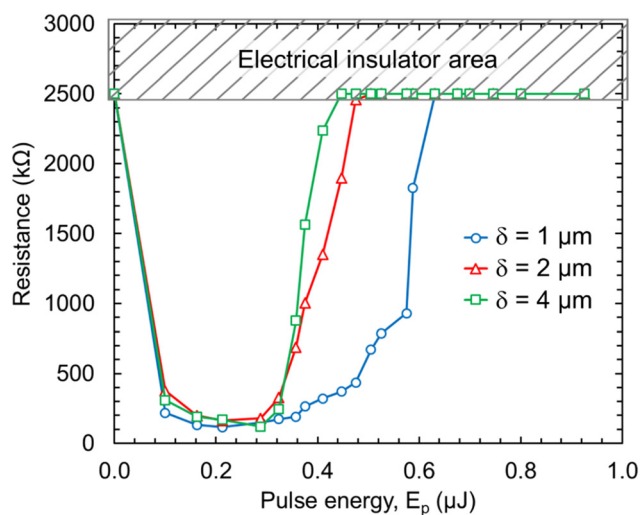


Fig. 2 Resistance measured by 4-point method in ZnO thin films after laser annealing as a function of the pulse energy for different hatching distances, as indicated. Lines are placed as eye-guides.



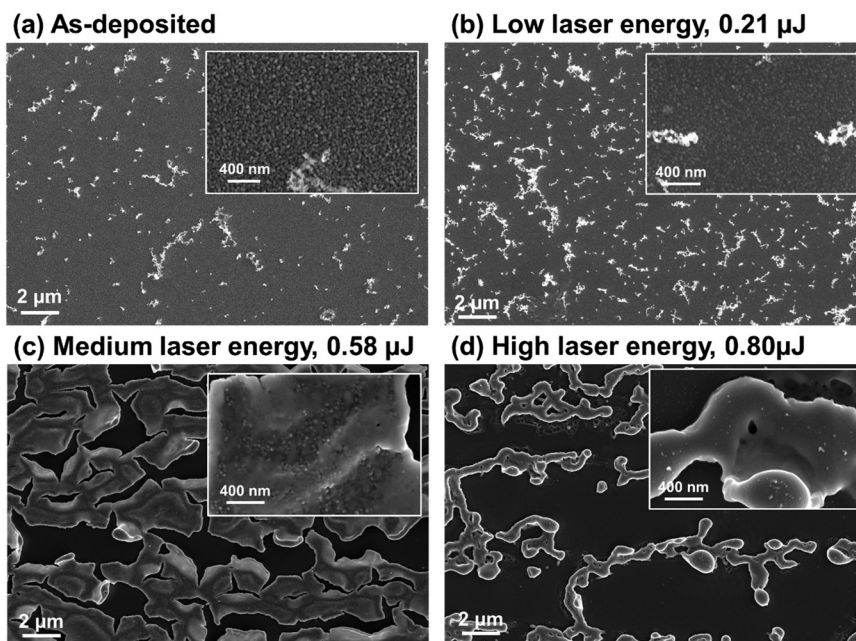


Fig. 3 SEM micrographs (in lens detector) of representative areas of the ZnO-film surface after laser annealing using  $\delta = 1 \mu\text{m}$  and different pulse energies: (a) as-deposited, (b)  $0.21 \mu\text{J}$ , (c)  $0.58 \mu\text{J}$  and (d)  $0.80 \mu\text{J}$ . Insets show higher magnification images.

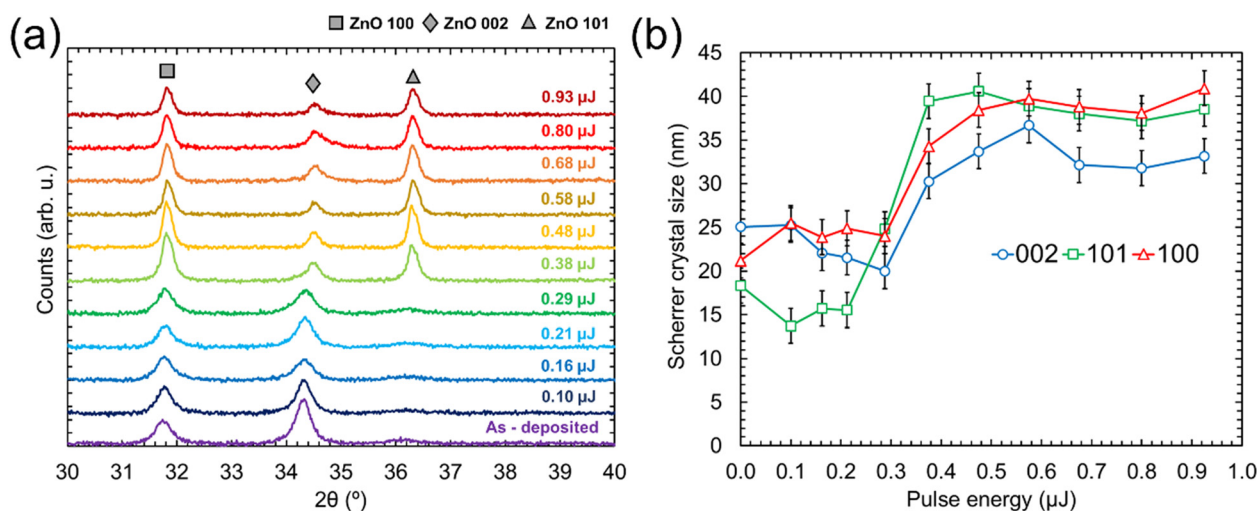


Fig. 4 (a) XRD patterns and (b) estimated crystal size calculated with Scherrer's equation, for laser-annealed ZnO thin films irradiated with varying laser pulse energies, ranging from 0.2 to 1.1  $\mu\text{J}$ . A hatching distance of  $\delta = 1 \mu\text{m}$  was used for these experiments.

thermal effects become more prominent and significant transformations are observed in the crystalline state. Specifically, the (100) and (101) reflections become predominant under these laser conditions. In contrast, the initially dominant (002) reflection becomes less prominent. These results demonstrate that picosecond laser annealing can induce significant alterations in the crystallinity of ZnO thin films.

At medium and high energy levels ( $\geq 0.38 \mu\text{J}$ ), the intense heating caused by laser irradiation leads to localized structural modifications in the ZnO thin films, resulting in alterations in the preferred crystalline orientation, which

shifts from (002) to (100) and (101). This energy threshold of  $0.38 \mu\text{J}$  per pulse agrees with the laser conditions that the ZnO domains start to separate causing the electrical resistance to increase.

These findings highlight the influence of laser energy and pulse duration on the thermal and structural dynamics during laser annealing processes. Understanding these dynamics is crucial for optimizing laser annealing techniques and controlling the desired structural modifications in thin film materials.

Fig. 4(b) shows a detailed examination of the estimated crystal size in response to the laser treatments performed





with different values of energy per pulse. The analysis of these data show that the crystals initially exhibit an average size of  $20 \pm 5$  nm, with minimal variability at low pulse energies. However, above the mentioned threshold of  $0.35 \mu\text{J}$  per pulse, the calculated crystal size increases up to  $38 \pm 5$  nm.

In the short-pulse regime using 300 ps laser radiation, the electron–phonon coupling time—which defines the characteristic duration for transferring energy from excited electrons to the ionic lattice—occurs on the order of a few picoseconds.<sup>54</sup> Therefore, these results agree with these theoretical predictions. If the pulse duration is above the characteristic phonon emission time (around 10 ps), a classical thermal heating of the ionic lattice is achieved. This leads to strong crystalline changes of the material towards the equilibrium texture orientation. In addition, these laser treatments produce an obvious crystal growth.

In essence, appropriate UV laser irradiation conditions induce electrical conductivity without producing holes or other type of detectable damage in ZnO SALD films.

In addition, for low (optimum) laser pulse energies, the thin film appears to undergo other type of modifications. Most oxides can lose oxygen from their structure under intense irradiation and high local temperatures,<sup>55–57</sup> conditions that occur during UV laser irradiation. These processes lead to the generation of oxygen vacancies and the desorption of trapped oxygen from the deposition process,<sup>5,53,56</sup> which are responsible for the observed enhancement in electrical behaviour. Moreover, as it was previously mentioned, since the laser wavelength used (355 nm) closely matches the energy of the ZnO band gap (3.6 eV), it may promote electron–hole pair generation, extracting more electrons from the valence band.<sup>8,44–46</sup> XPS experiments were performed to investigate the formation of oxygen vacancies in the ZnO films. However, the spectra of the laser-annealed and as-deposited samples were nearly identical, as shown in Fig. S2 of the SI. This suggests that the concentration of oxygen vacancies generated lies below the detection limit of XPS.

The obtained conductivity values in this study ( $11 \pm 6 \Omega^{-1} \text{cm}^{-1}$ ) are competitive with those reported in the literature for thicker thin films.<sup>58</sup> For undoped ZnO thin films, different fabrication methods including spray and plasma deposition yield electrical conductivities of  $6.74 \Omega^{-1} \text{cm}^{-1}$  for 460 nm films,<sup>59</sup>  $42 \Omega^{-1} \text{cm}^{-1}$  for 550 nm films,<sup>60</sup> and  $40 \Omega^{-1} \text{cm}^{-1}$  for 190 nm films.<sup>61</sup> Conductivities of  $1.4 \Omega^{-1} \text{cm}^{-1}$  have been reported for 600 nm La:ZnO films,<sup>62</sup> while higher values of up to  $345 \Omega^{-1} \text{cm}^{-1}$  have been achieved for 185 nm Al:ZnO films.<sup>5</sup> Other high temperature ( $>200^\circ\text{C}$ ) SALD ZnO thin films exhibit conductivity values in the range of  $20\text{--}250 \Omega^{-1} \text{cm}^{-1}$ .<sup>63–65</sup> For example, SALD ZnO thin films with a thickness of 210 nm show a conductivity of  $25 \Omega^{-1} \text{cm}^{-1}$  under UV irradiation. However, doping ZnO with aluminium can again decrease resistivity, yielding resistivity values as low as  $173 \Omega^{-1} \text{cm}^{-1}$ .<sup>53</sup> Although these technologies present

several advantages, the combination of laser processing and SALD provides an attractive alternative for the industrial-scale fabrication of high quality and performance ZnO thin films, where critical processes involving high vacuum technologies or doped thin films are avoided.

## 4.2. Resistance time evolution

Given the improvements in electrical conductivity induced by UV laser processing, a more in-depth study of the changes taking place during the laser irradiation process was performed using *in situ* and *operando* electrical resistance measurements, as explained in section 3.

Fig. 5 shows the temporal evolution of the electrical resistance of a ZnO thin film during and after the laser treatment. The laser processing parameters were:  $E_p = 0.3 \mu\text{J}$  per pulse,  $v_L = 800 \text{ mm s}^{-1}$ ,  $f_{\text{rep}} = 800 \text{ kHz}$  and  $\delta = 1 \mu\text{m}$ . The two regions that were described in section 3 can be clearly identified.

The elevated temperatures reached during the laser treatment, combined with the increased surface reactivity of the sample, result in an important increase in the resistance of ZnO films immediately after the laser treatment. Two regions have been indeed observed in the time evolution of the film resistance after laser annealing, as observed in the inset of Fig. 5. During the initial 45 s, the resistance increases at a faster rate, following closely a  $\sqrt{t-t_0}$  dependence, where  $t_0$  is the time when the laser treatment is stopped. In a second step, the resistance variation rate stabilizes, leading to a linear variation with rates in the range between  $0.1$  and  $1 \text{ k}\Omega \text{ s}^{-1}$ . These depend on the laser treatment conditions. This increase in the resistance values is maintained until the material becomes again fully insulating. This trend can be attributed either to the loss of oxygen vacancies<sup>66,67</sup> generated during the laser treatment, or to the subsequent

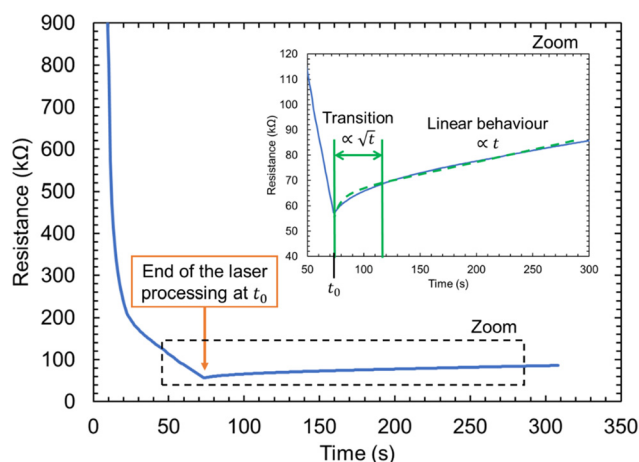


Fig. 5 *In situ* measurement of a ZnO thin film during and after laser annealing ( $\delta = 1 \mu\text{m}$  and  $E_p = 0.3 \mu\text{J}$ ,  $v_L = 1000 \text{ mm s}^{-1}$ ,  $f_{\text{rep}} = 800 \text{ kHz}$ ). The inset shows a zoomed view of the bottom part of the curve. The dashed lines in the inset correspond to square-root and linear fittings with time, as explained in the text.



reabsorption of oxygen. Both effects play a crucial role in the sample's electrical properties.<sup>5,45,46,56</sup>

The time-dependent variation of the resistance during the *operando* measurements is evaluated with the model presented in section 3. Based on the experimental results, the  $f_1(t^*)$  dependence introduced in eqn (4) can be modelled as:  $f_1z(t^*) = 1 + \alpha\sqrt{t^*}$  with an  $\alpha$  parameter ( $\alpha > 0$ ). Thus, the resistivity  $\rho_1(t^*)$  would be given by:

$$\rho_1(t^*) = \beta f_1(t^*)\rho_0 = \beta_0(1 + \alpha\sqrt{t^*})\rho_0 \text{ with } \beta_0(1; \alpha) > 0 \quad (7)$$

Therefore, the time evolution of the resistance of the laser treated area can be evaluated solving the following equation:

$$\frac{1}{R_{\text{treated}}(t)} = \int_0^{x'} \frac{e}{\beta_0 \rho_0 L} \frac{dx}{\left(1 + \alpha\sqrt{t - \frac{x}{v_{\text{trans}}}}\right)} \quad (8)$$

Solving eqn (8) using the procedure described in the Supplementary information,  $R_{\text{treated}}(t)$  follows this dependence:

$$\frac{1}{R_{\text{treated}}(t)} = \frac{-2 \cdot v_{\text{trans}} e}{\beta_0 \rho_0 L} \left( \frac{1}{\alpha} \sqrt{t} - \frac{1}{\alpha^2} \ln(1 + \alpha\sqrt{t}) \right) \quad (9)$$

Combining eqn (6) and (9), the total resistance of the sample at a given time  $t$  is described in eqn (10).

$$\frac{1}{R(t)} = \frac{1}{R_{\text{initial}}} \left[ 1 - \frac{v_{\text{trans}}}{W} \cdot t + \frac{2 \cdot v_{\text{trans}}}{\beta_0 W \alpha} \left( \sqrt{t} - \frac{1}{\alpha} \ln(1 + \alpha\sqrt{t}) \right) \right] \quad (10)$$

The measured *operando* electrical resistance reduction during UV laser annealing and the predicted calculations from the proposed model are compared in Fig. 6. The curve of the proposed model matches closely the trend observed on the experimental results, with fitting parameters  $\beta_0 = 9.7 \times 10^{-4}$  and  $\alpha = 3.14 \text{ s}^{-1/2}$  for these processing conditions.

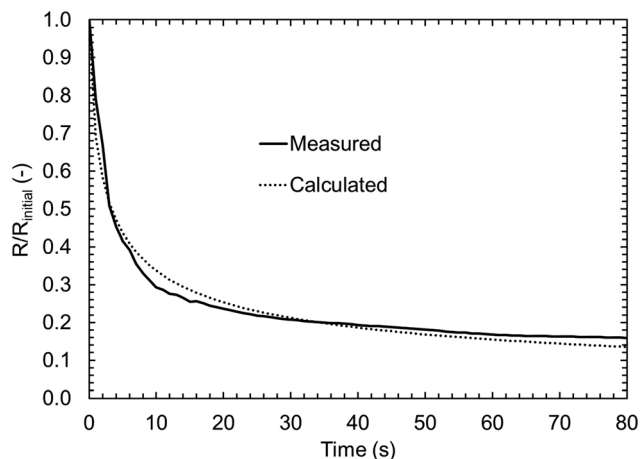


Fig. 6 Comparison of the time dependence of the relative resistance, measured and calculated for *operando* conditions during laser processing. The electrical measurement was performed while the laser processed area was increasing.

Overall, these measurements yield another significant outcome by demonstrating the selectivity inherent to laser processing, as it stands out as a prominent advantage of this processing route. Consequently, the changes in the electrical properties induced by the laser are limited exclusively to the irradiated area, with possible adverse effects observed in the heat-affected zone. In contrast, the electrical behaviour of the non-treated area remains unaltered under all circumstances.

Given the evolution of the resistance after the laser treatment, and in order to understand and exploit it, further experiments were performed. First we evaluated the reversibility of the process upon further laser treatments. A set of experiments was performed where the laser was alternatively turned on and off while the resistance ( $R$ ) was measured. In these experiments, the laser was turned on and it irradiated the ZnO until the full thin film was treated, reaching at that stage a minimum value ( $R_{\text{min}}$ ). This process took different times for a  $1 \text{ cm}^2$  sample depending on the laser conditions used, namely, 64, 32 and 16 s for the three hatching distances used of  $1 \mu\text{m}$ ,  $2 \mu\text{m}$  and  $4 \mu\text{m}$ , respectively. Afterwards, the laser was turned off during 64 s and the increase in the resistance was evaluated. This process was repeated several times and it is shown in Fig. 7.

The first notable outcome from these measurements is the full reversibility of the process, regardless of the hatching distance. For all evaluated hatching distances, similar minimum resistance values ( $R_{\text{min}}$ ) in the range of 120–160 k $\Omega$  were achieved after each cycle of laser annealing. Furthermore, the recovery time required to reach the lowest resistance value can be reduced from 64 seconds to 16 seconds by increasing the hatching distance from  $1 \mu\text{m}$  to  $4 \mu\text{m}$ . Additionally, the recovery time is independent of the oxygen concentration, indicating that it is primarily governed by the laser processing conditions rather than the sensing environment. Additionally, the ZnO thin films exhibit consistent behaviour even after several months of use.

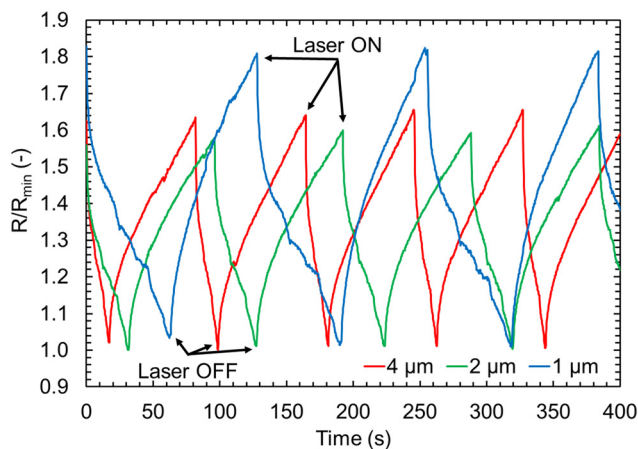


Fig. 7 Variation of resistance ( $R/R_{\text{min}}$ ) of ZnO thin film as a function of time when alternatively irradiating with the UV picosecond laser. The samples were maintained in ambient air.





This suggests good stability under cyclic operation and promising resistance to fatigue over extended periods.

Secondly, it was observed that after processing with hatching distances of 2  $\mu\text{m}$  and 4  $\mu\text{m}$ , the resistance increased up to 1.6 times the  $R_{\text{min}}$ . However, with a hatching distance of 1  $\mu\text{m}$ , the resistance increased to 1.8 times  $R_{\text{min}}$ . This indicates that the resistance increase rate is faster at lower hatching values. This phenomenon can be attributed to the longer processing time associated with smaller hatching distances, during which the thin film may enter in a more reactive state. Consequently, the absorption of oxygen species is accelerated, leading to a more rapid increase in the film's resistance.<sup>5</sup>

### 4.3. ZnO thin films for sensible oxygen detection

The demonstration of the reversibility and recovery of the initial electrical properties opens the door to various applications for these films, particularly in the development of transparent gas sensors. In such applications, the ability to regenerate and reverse processes provides a significant competitive advantage and is a crucial requirement for practical use. For example, a simple transparent oxygen sensor can be fabricated and regenerated by depositing a thin ZnO layer followed by rapid laser irradiation.

The results presented suggest that the time evolution of the electrical properties in laser-treated ZnO films may be intrinsically linked to the oxygen concentration in the surrounding atmosphere.<sup>5,8</sup> Therefore, it is worth exploring the possibility of using these ZnO films to detect oxygen levels.

Experiments were carried out where a laser annealing of the thin film was performed under vacuum and then the evolution of the electrical resistance was monitored under different atmospheres, namely,  $\text{O}_2$ ,  $\text{N}_2$  and Ar. Table 1 presents the composition of each atmosphere measured by gas chromatography. The values in italics are estimated from the measured data.

Fig. 8(a) illustrates how the film resistance evolves as a function of the gas concentration, controlled by pressure, within a chamber initially at 30 mbar and subsequently filled with different gases until reaching a pressure of 1 bar. It is assumed that the relative proportions of the gases remain constant with pressure changes, and only the number of moles of each gas varies accordingly. In this figure, resistance values are normalized relative to the minimum resistance achieved after laser treatment ( $R_{\text{min}}$ ). Notably, when argon or

nitrogen is introduced into the vacuum chamber, changes in pressure do not affect the rate of electrical conductivity loss, regardless of whether the pressure is increased or decreased. The resistance rates for argon and nitrogen are 0.45  $\text{k}\Omega\text{ s}^{-1}$  and 0.49  $\text{k}\Omega\text{ s}^{-1}$ , respectively, and, in the case of vacuum conditions, 0.24  $\text{k}\Omega\text{ s}^{-1}$ .

In these cases, the oxygen concentration is around 2.12% for the nitrogen atmosphere and 1.99% for the argon atmosphere. As argon is a heavier molecule than oxygen and nitrogen, the oxygen concentration should be slightly lower for the mentioned atmosphere. This reduced oxygen concentration is responsible for the slower resistance rate in the case of the argon environment.

In the case of vacuum conditions, the measurements are performed with the vacuum pump on, therefore, the amount of oxygen estimated is 1.04%. A residual nitrogen content of approximately 20% is measured in the oxygen-rich atmosphere. This is attributed to residual nitrogen remaining in the chamber and connecting lines, as well as possible leaks in the system during the chamber filling process.

However, when oxygen is introduced, there are evident changes in the rate of electrical conductivity variations. The greater the amount of oxygen introduced into the chamber, the higher the rate of the resistance increase. Additionally, it can be observed that when oxygen is removed from the chamber, the rate of loss decreases again, depending exclusively on the amount of oxygen in contact with the ZnO within the controlled atmosphere chamber.

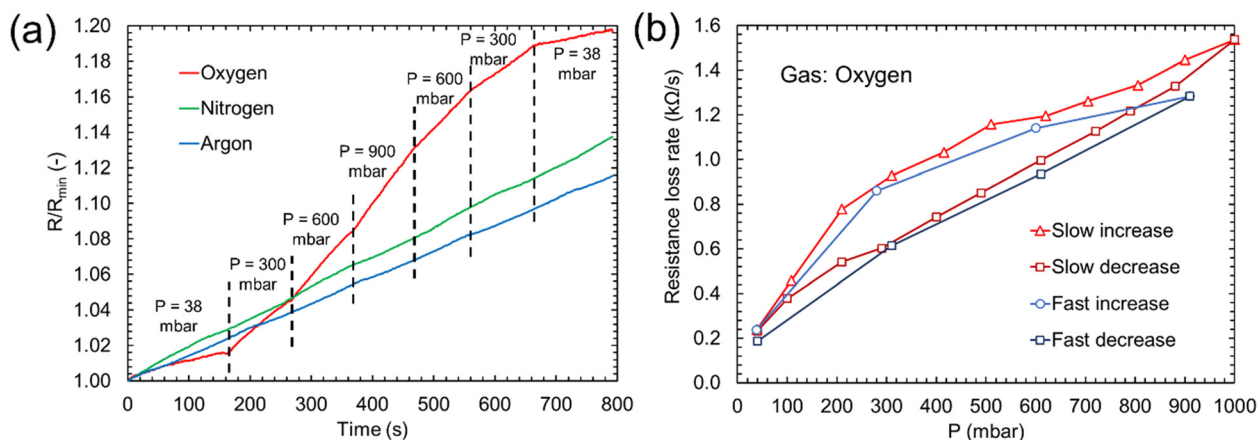
These results suggest that the rate of loss of the electrical resistance is closely related to the oxygen content, exhibiting some differences depending on the rate at which the amount of oxygen was increased or decreased (Fig. 8(b)). Different experiments were conducted to quantify this increase in the electrical resistance over time for varying oxygen concentrations. The rate of resistance increase was measured in an ascending process, gradually increasing the partial pressure of oxygen introduced from vacuum conditions, and in a descending process, progressively reducing the oxygen partial pressure from atmospheric conditions.

The rate of pressure increase/decrease has minimal impact on the resistance rate loss of the thin film, since values of similar order were measured for different increments of pressure (around 100 mbar for slow increments and 300 mbar for the faster ones). Under high-pressure conditions, variations in this rate become more noticeable. Specifically, the ZnO films exhibit higher resistivity when the pressure increment is applied more gradually. This observation is

**Table 1** Composition of the different treatment atmospheres. Gas compositions were measured by gas chromatography at 1 bar or estimated from the measured data (values in italics)

	Concentration of Ar	Concentration of $\text{O}_2$	Concentration of $\text{N}_2$
$\text{O}_2$ atmosphere	—	80.00%	20.00%
$\text{N}_2$ atmosphere	6.72%	2.12%	91.16%
Ar atmosphere	92.23%	1.99%	5.78%
Vacuum (38 mbar) atmosphere	—	1.04%	—





**Fig. 8** (a) Time variation of resistance of a ZnO thin film divided by the minimum resistance ( $R/R_{min}$ ). Time zero corresponds to the end of the laser treatment (30 mbar), and once finished, different gases were introduced into the chamber. The gas content is controlled by adjusting the pressure of the studied gas. (b) Resistance loss rate depending on the oxygen concentration inside the chamber.

consistent with the expected behaviour, as a slower increase imposes fewer kinetic limitations on the process, allowing for more controlled and uniform structural modifications within the film.

The reproducibility of this phenomenon is quite remarkable, as shown in Fig. 8(b), where the hysteresis behaviour remains nearly identical when the process is carried out using both shorter and longer pressure increment steps. The resulting curves almost overlap, further confirming the robustness of the observed response.

However, some hysteresis and differences between the pressure increase and decrease phases were observed. These differences are probably attributed to residual oxygen traces inside the vacuum chamber. Such traces are more likely to appear when gas is introduced gradually, possibly due to leaks in the seals or in the chamber, leading to higher resistance rate loss values. Conversely, when the pressure is progressively reduced by extracting gas from the chamber, it is also likely that any residual oxygen is being removed, reducing the resistance rate loss.

Further experiments must be conducted to confirm this hypothesis and verify whether it is indeed possible to reduce hysteresis, which would allow for the precise determination of oxygen present in the described controlled atmosphere environment by monitoring the rate of electrical conductivity loss in the ZnO thin films subjected to the present study. In this way, a transparent oxygen detection sensor based on laser-processed ZnO thin films could be developed. The sensor can be regenerated for reuse by repeating the laser treatment, even with high-speed processes on the order of 16 seconds.

Laser processing stands out as a particularly attractive technique for the industrial-scale fabrication of nanomaterials due to the almost unrestricted three-dimensional structuring capability especially for thin film processing, such as ZnO used in sensor applications studied in this work. Furthermore, laser techniques are highly

compatible with both, batch processing and large-area continuous manufacturing, offering significant advantages in scalability, production speed, and customization.<sup>68</sup> The ability to manufacture multiple units in a single run while minimizing setup times supports flexible and cost-efficient production workflows, making laser processing a key enabler for the transition from lab-scale prototyping to robust industrial manufacturing of ZnO-based sensing devices.

#### 4.4. Influence of the treatment atmosphere on laser processing of ZnO thin films

Based on previous studies, it is clear that the oxygen content in the atmosphere where ZnO thin films are measured significantly influences the temporal evolution of their physical properties. However, in all prior research, the laser processing step was conducted under vacuum conditions (low oxygen content). Therefore, it is essential to assess the influence of the atmospheric environment during laser processing to determine its impact on the final properties of laser-annealed ZnO thin films.

Fig. 9 shows the evolution of the electrical resistance over time after laser processing of the thin films under different atmospheres: ambient air, argon at atmospheric pressure, and vacuum at 38 mbar. Since the resistance of ZnO increases rapidly in the first few seconds following laser irradiation, each sample was kept in the corresponding processing atmosphere for 10 minutes to allow the resistance to stabilize and reach a quasi-stationary regime.

Subsequently, the resistance evolution shown in Fig. 9 was measured under ambient air conditions, regardless of the atmosphere used during the laser processing step. This approach allows for a consistent comparison of the long-term electrical behaviour of the films, while still capturing the influence of the different atmospheres during processing.

On the one hand, regardless of the treatment atmosphere, the electrical resistance is observed to increase in an



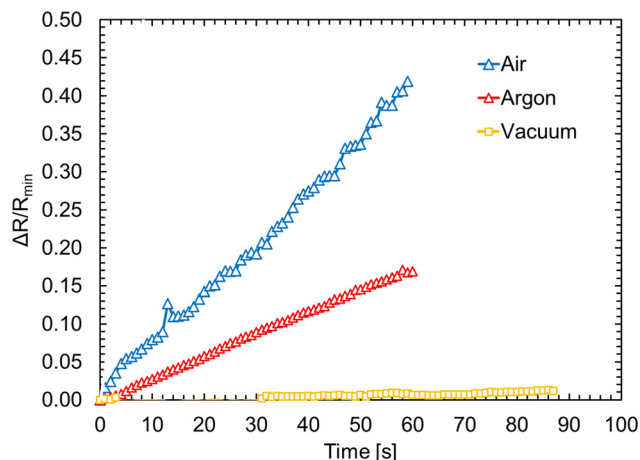


Fig. 9 Evolution with time of the electrical resistance of ZnO thin films after UV laser annealing ( $E_p = 0.3 \mu\text{J}$ ,  $\delta = 1 \mu\text{m}$ ) performed in different atmospheres, including air and argon at atmospheric pressure, and at 38 mbar in vacuum conditions.

approximate linear fashion as a function of time, in accordance with previous experiments. Moreover, these measurements reveal that, when the laser treatments are performed in vacuum, the variation rate is much lower than when they are performed in air or in argon: 1.74, 0.73 and  $0.02 \text{ k}\Omega \text{ s}^{-1}$  are, respectively, the values obtained when the samples were processed in air, argon and vacuum.

The surface of the ZnO thin films processed in air atmosphere has proven to strongly interact and react with different gases, especially nitrogen and hydrogen species, causing changes in its resistance.<sup>8</sup> The presence of nitrogen and oxygen in the processing atmosphere develops surface dynamics that accelerate the rate of electrical conductivity loss. When processing in argon, a noble gas, the increase in resistance is mitigated compared to processing in air. However, the desorbed oxygen from the film is not evacuated, facilitating reabsorption over time and leading to an intermediate increase rate in resistance. In contrast, processing the sample under dynamic vacuum conditions effectively evacuates the desorbed oxygen and favours preservation of the oxygen vacancies generated during the laser treatment. These phenomena appear to stabilize the surface reactivity, significantly minimizing the temporal increase in resistance when the film is re-exposed to air.

These results open the possibility to introduce a last step to preserve the favourable laser induced properties. This step would involve the *in situ* deposition of a protective coating, such as  $\text{Al}_2\text{O}_3$ , immediately after laser processing, and under vacuum conditions, as it has been shown to hinder oxygen exchange with the atmosphere.<sup>5</sup> This would ensure that the laser-irradiated ZnO films would not be exposed to oxygen, thereby maintaining the low resistivity values induced by the laser process. Although this approach is not currently feasible with the equipment and conditions available in our laboratory, the findings highlight its potential for producing ZnO-based thin films for applications requiring conductive coatings.

These results illustrate the significance of the treatment and measurement atmosphere and the laser processing parameters in ZnO thin films, as they play a crucial role in the reorganization of oxygen vacancies and other chemical changes in this material.

## 5. Conclusions

The work reported here demonstrates that laser annealing can tune and modify the resistivity of 90 nm thick ZnO films deposited by SALD. The best electrical performance achieved on these films, after appropriate laser processing conditions yield an electrical resistivity value of  $(9 \pm 2) \times 10^{-2} \Omega \text{ cm}$ . A wide range of medium laser pulse energies and overlap help maintain the excellent electrical properties of the thin films. If the energy exceeds a certain pulse energy threshold, a progressive loss of the induced electrical properties is observed. This is caused by the deterioration of the thin film integrity, with the initial formation of connected ZnO domains and the eventual loss of continuity between them, upon further energy per pulse increments.

Additionally, an analysis of the applied laser process and the evolution of the electrical resistance of the films as a function of time was performed. A resistance model that reproduces the laser processing experiments and the observed changes on the resistivity over time of the ZnO thin films is herein proposed. After the improvement of the electrical characteristics of the coatings by UV laser irradiation, the electrical resistance starts increasing in a two-stage process: within the first seconds a rapid increase appears to end in a linear trend until an insulating behaviour is reached.

However, subsequent laser annealings have proven to recover the low initial resistivity values obtained. Additionally, the recovery time of a  $1 \text{ cm}^2$  sample can be adjusted and reduced to 16 seconds by increasing the hatching distance to  $4 \mu\text{m}$ , thus reducing the overlap between two laser lines.

Subsequently, the rate of loss of the electrical resistance is observed to be highly dependent on the oxygen concentration in the surrounding atmosphere. The greater the amount of oxygen introduced into the chamber, the higher the rate of the resistance increase. Some hysteresis and differences between the pressure increase and decrease phases were observed and they were attributed to residual oxygen traces inside the vacuum chamber. Ultimately, the laser annealed ZnO thin films were successfully tested as transparent, room-temperature oxygen sensors with a detection limit of 30 mbar constrained by our measurement set-up.

Finally, it has been observed that the treatment atmosphere also affects the rate of electrical resistance decay of the ZnO films after the treatment. A vacuum atmosphere has been shown to reduce the rate of resistance loss more effectively than argon or air atmospheres. Our findings suggest a promising method to preserve laser-induced properties





through the *in situ* deposition of a protective coating under vacuum conditions. This approach could enable the production of ZnO-based conductive thin films.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Supplementary information: Transmittance of laser annealed ZnO, XPS of laser annealed and as-deposited ZnO, and model development. <https://doi.org/10.1039/D5LF00076A>.

Data are available at: <https://doi.org/10.5281/zenodo.14604134>.

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