Characterization of Zinc Oxide Thin Film Gas Sensors Fabricated by Pulsed-Laser Deposition

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In this work, pulsed-laser deposition (PLD) technique was used to prepare pure ZnO thin films on glass substrates. All prepared films were polycrystalline with hexagonal structure. The grain size and surface roughness were found to increase with increasing number of laser pulses. Optical properties showed that the films have high transmission in the visible region (>80%), in addition to a decrease in the transmittance with increasing number of laser pulses. The energy gap value was nearly 3.25 eV for all films. Based on the grain size of the film, 400 pulses were selected to make a gas sensor from pure ZnO films. These films showed different responses for sensing NO_2 and H_2S gases at three different operating temperatures (100, 150, and 200°C). The pure ZnO film sensor showed a sensing sensitivity for NO_2 gas of 90.24% with a response time of 25.2 s at an operating temperature of 200°C, while the maximum sensitivity for H_2S gas was 22.89% with a response time of 12.6 s at an operating temperature of 150°C.

***Keywords*:** Pulsed-laser deposition; Zinc oxide; Hexagonal structure; Gas sensors
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1. Introduction

The need for a safe working environment free from poisonous gases and indoor pollutants has led to an increase in interest in gas sensors. The inhalation of these gases is not safe for humans above the permissible limit; therefore, it has become necessary to identify the presence of these gases [1] and develop fast-responding, highly sensitive, careful gas sensors [2]. Metal oxide semiconductor-based gas sensors are one of the finest choices due to their multiple advantages, such as low cost, smaller size, quick reaction, simple production, and excellent compatibility with microelectronic processing. [3]. One of the primary advantages of metal oxide semiconducting nanoparticles is their high surface-to-volume ratio. Because sensing response is strongly dependent on the surface of the materials exposed to gases, the sensor based on thin film nanostructures is expected to perform better than the bulk sensor [3].

Semiconducting metal oxide sensors such as SnO_2, TiO_2, ZnO, In_2O_3, Fe_2O_3, and WO_3 have been used to detect both reducing (NH_3, CO, H_2S, CH_4, C_3H_8) and oxidizing (NO_2) gases [4]. Zinc oxide (ZnO) is more suitable for gas sensing applications due to its physical, chemical, and thermal stability. It has a significant exciton binding energy of 60 meV and a wide band energy gap of 3.37 eV at ambient temperature [5]. It has many uses in many optoelectronic applications due to its remarkable electrical and optical qualities, such as ultraviolet light-emitting diodes [6], thermal and optical temperature sensors [7], gas sensors [8], and dye-sensitive solar cells [9].

There are various deposition methods for preparing nanocrystalline ZnO films, including the sol-gel method [10], spray pyrolysis [11], hydrothermal growth [12], chemical vapor deposition [13], electron beam evaporation [14], and pulsed-laser deposition [15]. Pulsed-laser deposition is the most effective method among them for producing nanocrystalline ZnO films at a wide variety of deposition parameters [15,16].

By controlling the electro-physical and structural characteristics of ZnO films, the gas sensing characteristics of the films can be enhanced by the selection of the deposition parameters, such as the laser energy, repetition rate, pressure of the oxygen, temperature and type of substrate, type and ratio of the dopants, time and number of pulses, distance between target and substrate, thickness of thin films, and annealing conditions [15-17].

2. Experimental Part

ZnO thin films were deposited on glass substrates using pulsed-laser deposition method. The target was fabricated from ZnO powder with a purity of 99.9%, which was pressed using a hydraulic compressor of 5 tons for 5 minutes to obtain circular discs of 2 g in weight, 10 mm in diameter, and 2 mm in thickness, which are suitable for preparing the films. The glass substrates were cleaned by ultrasonic, then by ethanol and subsequently positioned on a holder in front of the target surface. The distance between the substrate and the target was 3 cm. The films were produced in a vacuum chamber at a pressure of 10^{-3} mbar. The Nd:YAG laser system is operated at a wavelength of 1064 nm, with a repetition rate of 6 Hz, energy of 600 mJ, and different number of laser pulses (200, 400, and 600 pulses). The prepared films were annealed in an oven at 450 °C for 2 hours. The x-ray diffraction (XRD), atomic force microscopy (AFM), field-emission scanning electron microscopy (FE-SEM), and the UV-visible spectrophotometry were used to study the effect of the number of laser pulses on the characteristics of the prepared ZnO films. After that, the optimum number of pulses was determined and

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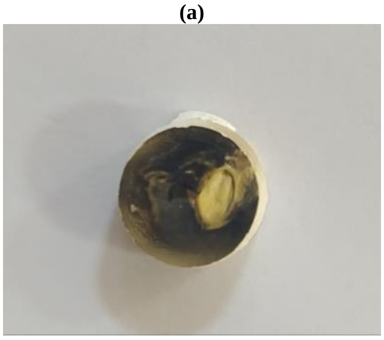
selected to fabricate gas sensing elements for NO_2 and H_2S gases at different temperatures. Figure (1) shows ZnO target before and after irradiation with laser.

(a)



(b)

Fig. (1) ZnO target (a) before and (b) after laser irradiation

3. Results and Discussion

Figure (2) shows the XRD patterns of pure ZnO films deposited on glass substrates by PLD method. The results showed that the films have hexagonal polycrystalline wurtizte structure [18]. The crystal planes (100), (002), and (101) indicate the ZnO with preferred orientation at 2θ=31.8° in the (100) plane, in addition to the appearance of new planes (102), (110), (103) when the number of pulses was increased to 600 pulse. These results are consistent with the standard ICCD card 00-036-1451 for ZnO. It was noted that the number of planes increases with increasing number of laser pulses [18], as shown in table (1), and increasing number of laser pulses produce sharper and more powerful diffraction peaks, suggesting higher film crystallinity.

The surface topography of pure ZnO samples was studied using AFM. Figure (3) shows the 2D and 3D AFM images of ZnO films deposited at different numbers of laser pulses. Table (2) shows the values of the average grain size, roughness and root mean square (RMS) of ZnO films prepared using 200, 400 and 600 laser pulses. Increasing the number of laser pulses to 600 pulses lead to increase the roughness due to the formation of larger grains in the ZnO thin film [19], while the grain size was decreased to 72.57 nm for the sample prepared using 400 laser pulses, which is beneficial for the sensor as the small particle size increases the sensitivity to gas [20].

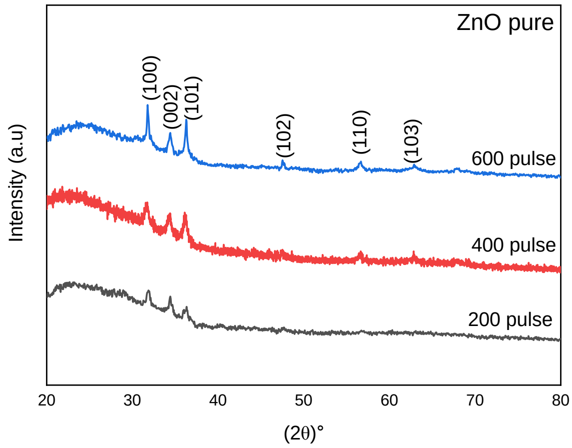
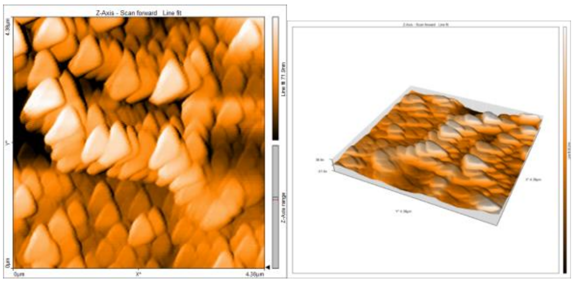


Fig. (2) XRD patterns of ZnO thin films prepared using different numbers of laser pulses (200, 400, and 600 pulses)

Table (1) XRD parameters of ZnO thin films prepared using different numbers of laser pulses

No. of pulses	2θ (deg)	FWHM (deg)	$d_{hkl.}$ (Å)	C.S. (nm)	(hkl)
200	31.87	0.2952	2.80806	28.0	(100)
	34.46	0.3936	2.60224	21.1	(002)
	36.25	0.7872	2.47805	10.6	(101)
400	31.87	0.4061	3.01821	20.3	(100)
	34.46	0.4365	2.64541	19.1	(002)
	36.25	0.4616	2.51189	18.1	(101)
	56.03	0.177	1.64006	50.8	(110)
	62.79	0.4394	1.47858	21.2	(103)
600	31.81	0.1476	2.81336	56.0	(100)
	34.39	0.3936	2.60774	21.1	(002)
	36.28	0.1968	2.47572	42.5	(101)
	47.59	0.2952	1. 91056	29.4	(102)
	56.63	0.5904	1.62529	15.3	(110)
	62.87	0.1808	1.47809	51.5	(103)



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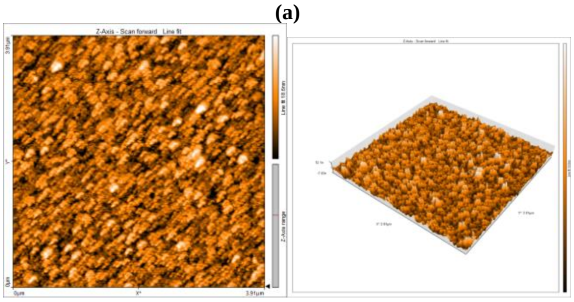

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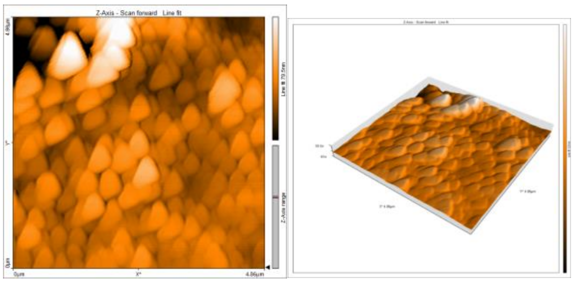


(c)

Fig. (3) AFM images of ZnO thin films prepared using different numbers of laser pulses (a) 200, (b) 400, and (c) 600

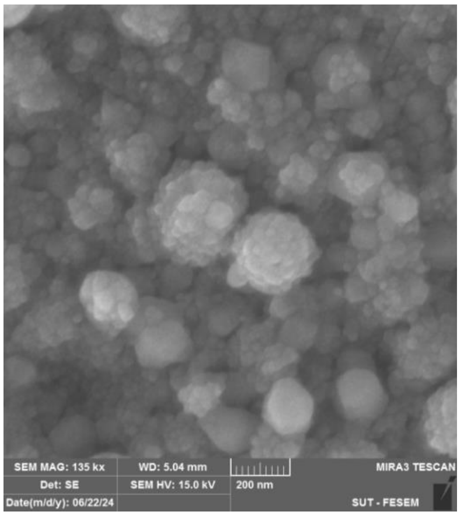
Table (2) AFM parameters for ZnO thin films prepared using different numbers of laser pulses

No. of Pulses	Roughness Average (nm)	R.M.S. Roughness (nm)	Average Grain Size (nm)
200	20.19	27.02	104.1
400	4.927	6.299	72.57
600	21.71	25.87	135.5

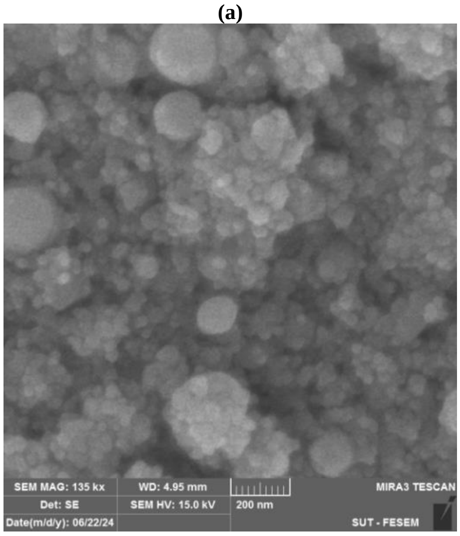
Figure (4) shows FE-SEM images of pure ZnO films deposited using 200, 400, and 600 laser pulses. Spherical and white ZnO nanoparticles were randomly distributed. Also, the ZnO nanoparticles were compact and uniformly arranged, with virtually random forms. The particles in the prepared sample varied in size, with the larger particles consisting of tiny crystals [21]. This signifies that the primary nanocrystals merge to form larger particles [22].

The optical characteristics of the deposited ZnO films were examined in the wavelength range of 300-1100 nm, as shown in Fig. (5). It shows that all ZnO films become transparent for the longer wavelengths (λ>380nm). Also, it was found that they have a high optical transmittance in the visible region (>80%). Their high transmittance in visible range make these films an excellent candidates for transparent window in thin film solar cells [18,23]. In addition, the transmittance value exhibits a slight decrease as the number of laser pulses is increased. This result agrees to previously published results [18]. The optical energy gap was found to be direct and its value is nearly 3.25 eV for all films, as shown in Fig. (6). Therefore, ZnO thin films were used as transparent conductive oxide (TCO) in many optoelectronic applications [23].

The optimum ZnO film samples were examined for gas sensing using NO_2 and H_2S gases at different operating temperatures. Figure (7) shows the resistance as a function of time at 100, 150, and 200°C. This figure shows that the film's resistance increases when exposed to NO_2 gas (gas ON), and it drops off when there is no gas (gas OFF). The explanation for this behavior is connected to the NO_2 gas having an ionic interaction with the surface adsorption oxygen, where the electron on the oxygen is taken from the semiconductor and causes its conductivity to drop, thereby increasing the resistance [24].



(a)



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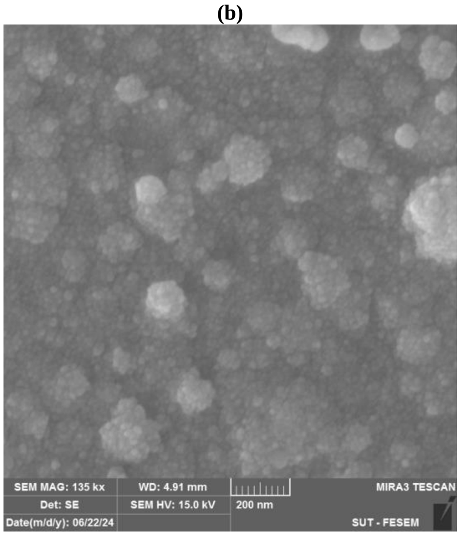


(c)

Fig. (4) FE-SEM images of ZnO thin films prepared using different numbers of laser pulses (a) 200, (b) 400, and (c) 600

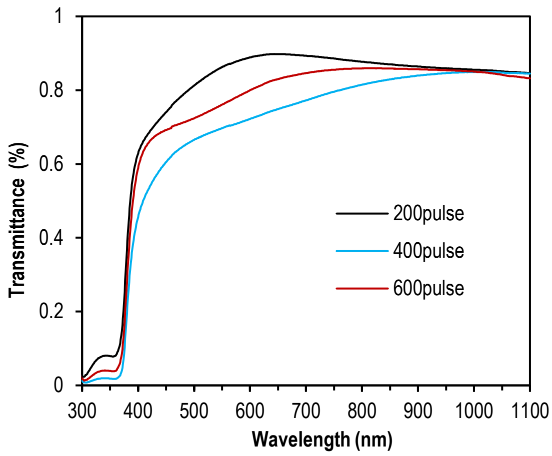


Fig. (5) Optical transmission spectra for ZnO films prepared using different numbers of laser pulses

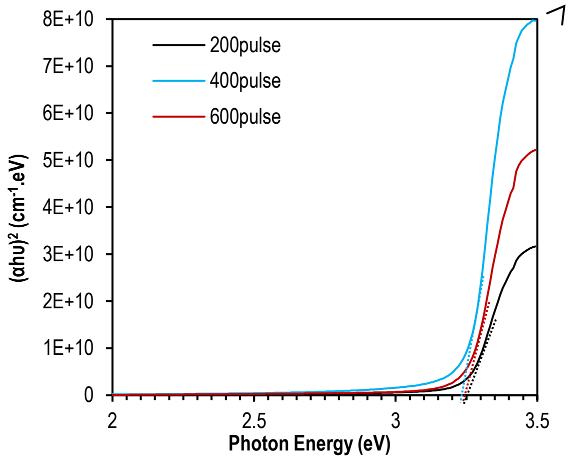


Fig. (6) Determination of energy gap for ZnO films prepared using different numbers of laser pulses

Figure (8) shows the sensitivity of ZnO films using NO_2 gas and the results show that the sensitivity increases as the operating temperature increases, which is consistent with [25], while the response and recovery time decrease with increasing temperature as shown in table (3). The typical response time of ZnO-based gas sensor may be a minute or shorter. Other characteristics that may affect response time are NO_2 flow rate, temperature, and analyzer gas pressure [26].

Table (3) Sensitivity, response time, and recovery time of pure ZnO film gas sensor for NO_2 test gas at different temperatures

Temperature (°C)	Response time (s)	Recovery time (s)	Sensitivity (%)
100	29.7	69.3	51.28
150	27.9	52.2	76.24
200	25.2	42.3	90.24

The sensing characteristics of the prepared samples to H_2S, a highly flammable and toxic gas, were studied at different temperatures. Figure (9) shows that film's resistance decreased with the presence of gas due to electron trapping by the gas, where the concentration of hole carriers increased significantly. Based on the measured values, the highest sensitivity to the gas was at 150°C, reaching 22.89%. Although the highest sensitivity value was at 150°C, the response was faster at 200°C, with a response time of 7.2 s, as shown in Fig. (10) and table (4).

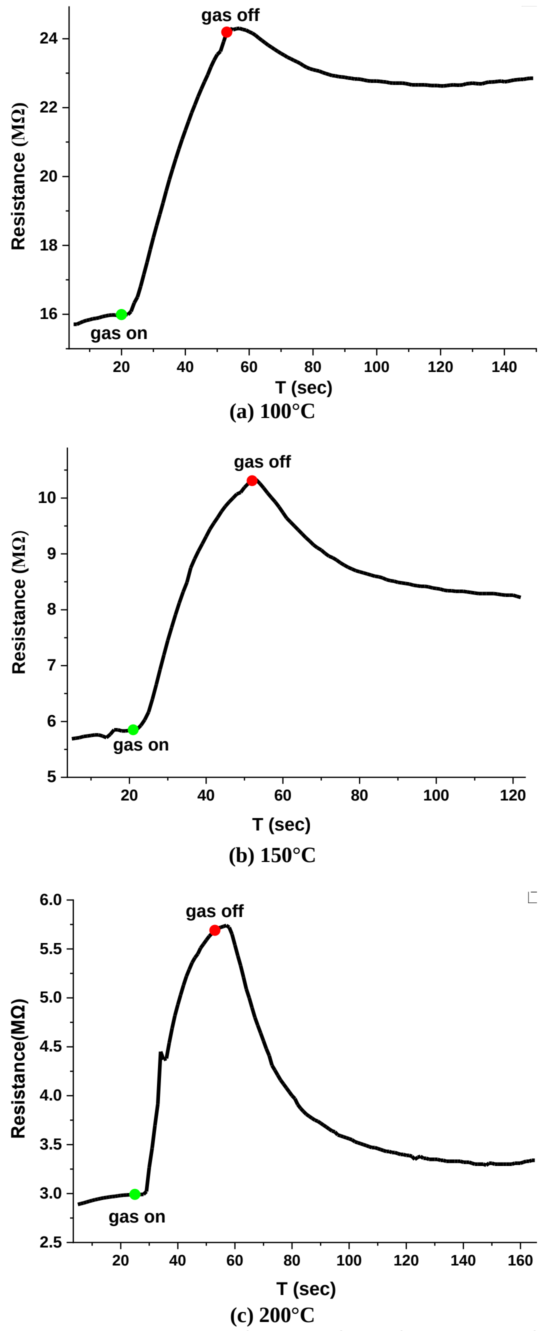


Fig. (7) Film resistance as a function of time for pure ZnO film deposited using 400 laser pulses at (a) 100°C, (b) 150°C, (c) 200°C using NO_2 as a test gas

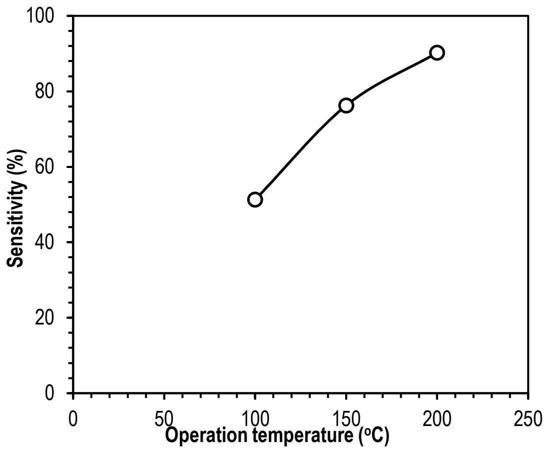
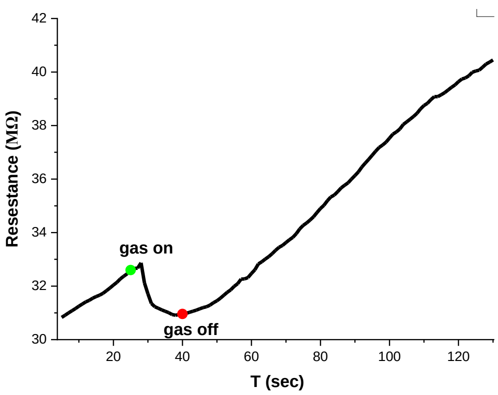


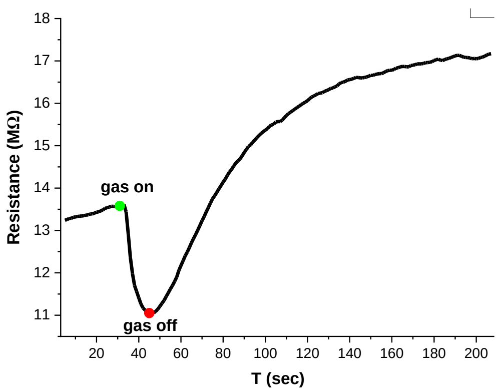
Fig. (8) Sensitivity with operating temperature for ZnO gas sensor using NO_2 as a test gas

Table (4) Sensitivity, response and recovery time for pure ZnO gas sensor at different temperature using H_2S as a test gas

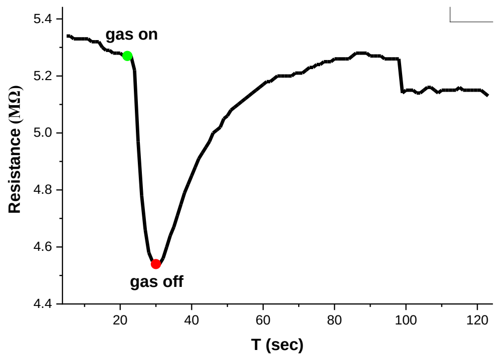
Temperature (°C)	Response time (s)	Recovery time (s)	Sensitivity (%)
100	13.5	54	5.29
150	12.6	49.5	22.89
200	7.2	63	16.08



(a) 100°C



(b) 150°C



(c) 200°C

Fig. (9) Film resistance as a function of time for pure ZnO film deposited using 400 laser pulses at (a) 100°C, (b) 150°C, (c) 200°C using H_2S as a test gas

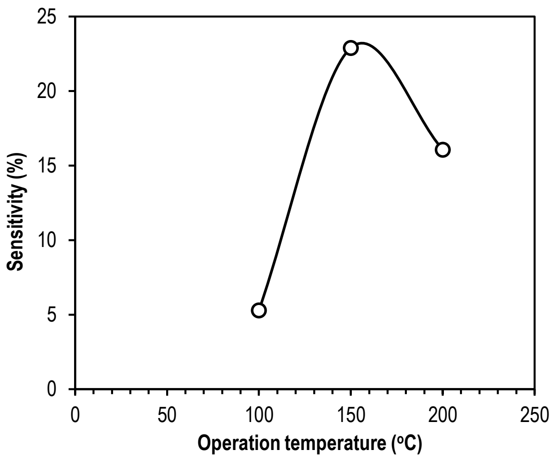


Fig. (10) Sensitivity with operating temperature for ZnO gas sensor using H_2S as a test gas

4. Conclusion

ZnO films prepared by PLD on glass substrates showed that thy have a polycrystalline hexagonal wurtzite structure, while the optical properties showed a decrease in the transmittance with increasing number of laser pulses. The lowest grain size was obtained at 400 pulses, which is beneficial for fabricating the gas sensor. The effect of microstructure on the response of ZnO to NO_2 and H_2S gases was investigated and showed good response to both gases (oxidant and reducer) at different temperatures. It was also found that increasing the operating temperature had a positive effect on the sensitivity and response time.

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