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# Synthesis and Characterization of ZnO Thin Films and Study of Thermal Annealing Effects on Their Performance in Gas Sensing

ZnO thin films (0.1 M) were deposited on glass substrates using the chemical spray method and annealed at 450°C and 600°C to study the effect of thermal treatment. Field-emission scanning electron microscopy (FE-SEM) revealed grain growth from 12 nm to 24 nm with increasing temperature, indicating enhanced atomic mobility and surface uniformity. X-ray diffraction (XRD) confirmed improved crystallinity and reduced defects, while optical analysis showed a band gap widening up to 4.6 eV. Gas sensing for NO<sub>2</sub> improved with annealing, showing higher sensitivity and shorter response and recovery times, whereas non-annealed films exhibited inherently fast response. The enhancements are attributed to larger grains, better crystallinity, and more active adsorption sites

**Keywords:** Gas sensing; Zinc oxide; Thin films; Thermal annealing

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## 1. Introduction

Zinc oxide (ZnO) is an interesting semiconducting material due to its specific electronic, optical, and chemical properties [1]. More interestingly, the direct band gap of 3.37 eV of is attractive for optoelectronic applications in the visible to ultraviolet spectral ranges [2-4]. Moreover, hexagonal ZnO has high excitation binding energy (60 meV) and a high dielectric constant that makes it a suitable material for many technologies [5]. The combination of these features makes ZnO suitable for a wide range of applications in several different fields of the sciences, such as optoelectronics, or energy conversion and sensing systems [6].

ZnO which have been developed as nanomaterials, especially the ones with nanoscale structures, are among the most prospective materials for a variety of industrial and scientific applications [7]. The combination of these features make ZnO nanoparticles not only suitable but also suitable for numerous applications like photo catalysis, solar energy conversion, chemical sensors, biomedicine [8-10].

Chemical spray deposition [6], one of the many available techniques for synthesizing ZnO nanostructures, has received a significant degree of attention. This method has many advantages, such as deposition of thin, high quality and uniform layer of ZnO on various substrates [11]. In this method, a precursor solution containing metals is sprayed on the substrate at the appropriate temperature for the formation of ZnO nanostructures. [12].

In this context, we outline past and ongoing synthesis and characterization of macro-and

nanostructures of ZnO primarily to enhance the operation of devices and their potential sensing applications [13].

The ongoing research of highly effective general synthesis methods like chemical spray deposition will keep enhancing the characteristics and scalability for ZnO-based devices, which is promising for novel applications in various fields [14,15].

## 2. Experimental Procedure

Zinc oxide (ZnO) thin films were deposited on glass substrates using the chemical spray pyrolysis technique. The precursor solution was prepared by dissolving zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) in distilled water to obtain a concentration of 0.1 M. The solution was stirred at room temperature until complete dissolution to ensure homogeneity.

Standard Soda–lime glass slides (7.6×2.6×0.1 cm<sup>3</sup>) were used as substrates. Prior to deposition, the glass slides were sequentially cleaned with detergent, distilled water, ethanol, and acetone, followed by drying in air to remove any surface contaminants. The cleaned substrate was placed horizontally on an electric heater. The heater surface was meticulously cleaned to remove any residual particulates before deposition. Substrate positioning was carefully adjusted to ensure uniform heating across its surface. The vertical movement of the spray solution and the distance between the spray nozzle and the substrate were precisely controlled, with an optimal nozzle-to-substrate distance of 28 cm.

The substrate was placed on the heater for 15-20 minutes to reach thermal equilibrium. Once the target deposition temperature of  $350 \pm 10$  °C, monitored by a digital thermocouple, was attained, the spray valve was opened, and the precursor solution was atomized through a 22 mL nozzle at a controlled flow rate. Each spray cycle lasted 5 s, followed by a 55-s interval between sprays to prevent rapid cooling and to allow the substrate to preheat between successive sprays.

After completion of the spraying process, the heater was turned off while maintaining the deposited film on the substrate. This gradual cooling step facilitates the completion of chemical reactions associated with crystallization and grain growth, minimizing the risk of film cracking due to thermal shock.

Post-deposition annealing was conducted in a closed oxidation furnace under a continuous flow of oxygen gas at 400 scfm. The annealing temperatures were set at 450 °C and 600 °C, and the process lasted for 2 hours. Following annealing, the samples were allowed to cool naturally inside the furnace to room temperature over 24 hours, ensuring a controlled cooling process to preserve film integrity.

### 3. Results and Discussion

At a molar concentration of 0.1 M, as shown in figures (1) and (2), as the annealing temperature increases, the intensity of the XRD peaks increases. The intensity was found to increase with higher annealing temperatures, which is in agreement with [17]. This is due to the fact that thermal annealing removed some of the defects and imperfections present after the growth process and led to the reorganization of the crystalline grains, allowing the grains to gain enough energy to grow and align within the crystal lattice, as shown in tables (1) and (2). These results match well with the open crystallographic database (COD) number (96-101-1260).

Table (1) Structural properties of ZnO NPs for (0.1M) 450°C

$2\theta$ (deg.)	(hkl)	FWHM (deg.)	$d_{hkl}$ Exp. (Å)	Crystallite Size (nm)	Average Crystallite Size (nm)
31.78	100	0.72	2.81	12.4	12.96
34.42	002	0.55	2.60	16.1	
36.25	012	0.60	2.47	14.8	
47.54	110	0.78	1.91	11.2	
62.75	013	0.85	1.63	10.3	

Table (2) Structural properties of ZnO NPs for (0.1M) 600°C

$2\theta$ (deg.)	(hkl)	FWHM (deg.)	$d_{hkl}$ Exp. (Å)	Crystallite Size (nm)	Average Crystallite Size (nm)
31.74	100	0.38	2.86	23.1	24.82
34.40	002	0.26	2.60	34.2	
36.23	012	0.30	2.47	29.6	
47.52	110	0.44	1.82	20.4	
62.74	013	0.55	1.48	16.8	

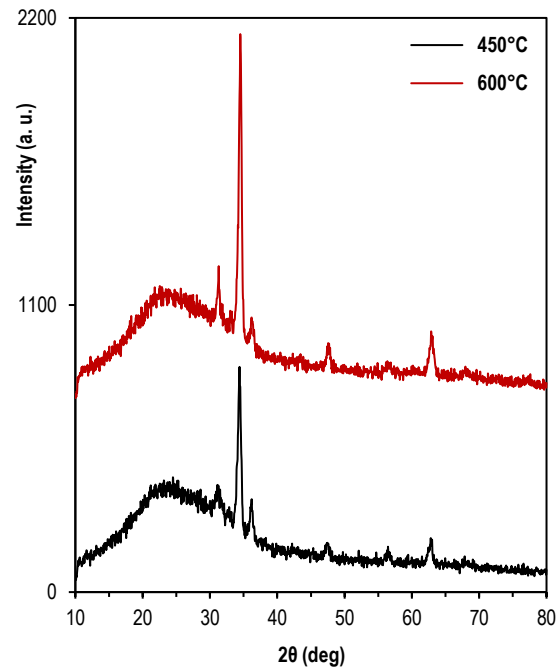


Fig. (1) XRD patterns of ZnO thin films after annealing at two different temperatures (450°C and 600°C)

Figure (2) shows FE-SEM images of ZnO films deposited and annealed at 450 to 600 °C at two different molar concentrations at a magnification of 200 nm. These images show that the ZnO films are in the form of bundles of nanocrystals and contain multiple clusters. These results can be explained by the nucleation and growth process. The results show that at 600 °C, the grain size decreases at a concentration of 0.1 M and increases with increasing annealing temperature. This is due to the fact that at a certain point in the annealing temperature, phonon vibrations make the surface more uniform. This is consistent with the results of reference [18].

In Fig. (3), the optical absorption spectrum in the wavelength range (200-800 nm) is studied, showing the absorption spectra of zinc oxide films before and after annealing. Absorption measurements for the zinc oxide films before and after annealing were obtained using a UV-visible spectrophotometer. The spectrum shows that absorption decreases with increasing wavelength, indicating that the incident photons are unable to excite electrons and transfer them from the valence band to the conduction band, as the photon energy is lower than the energy gap in semiconductors. In this context, the effect of the annealing process played a significant role in increasing the absorption, where an increase in absorption was observed at a concentration of 0.1 M and an annealing temperature of 600°C, which is consistent with results of references [19,20].

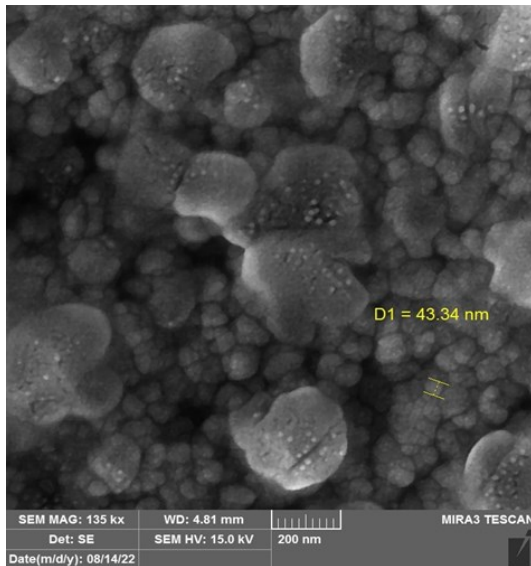
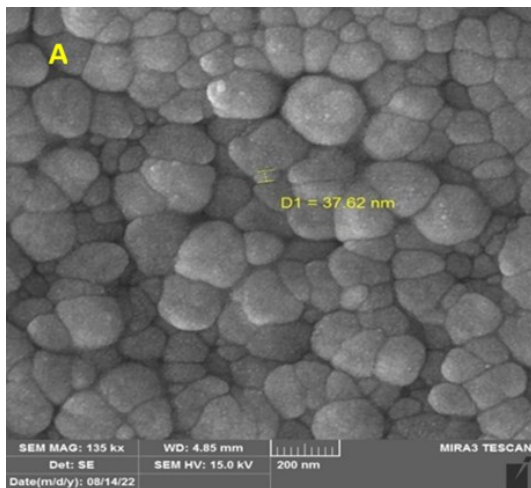


Fig. (2) FE-SEM images of ZnO thin films after annealing at two different temperatures (450°C and 600°C)

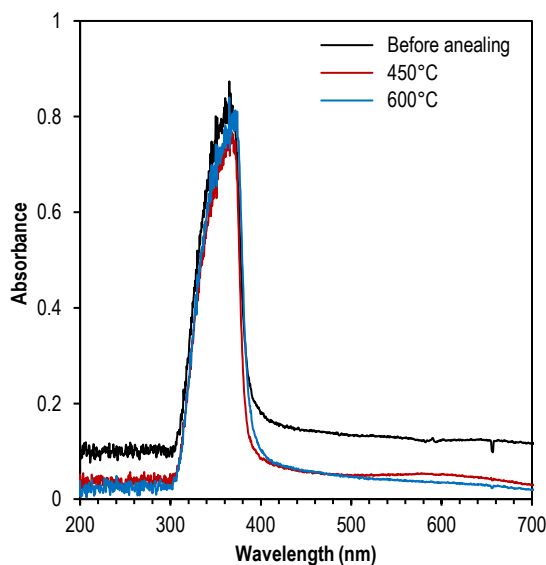


Fig. (3) Absorption spectra of ZnO thin films before and after annealing at two different temperatures

In Fig. (4), the energy band gap of 3.2 eV was not changed after thermal annealing since no changes in the positions of the atoms in the crystal lattice were induced, while the particle size became larger.

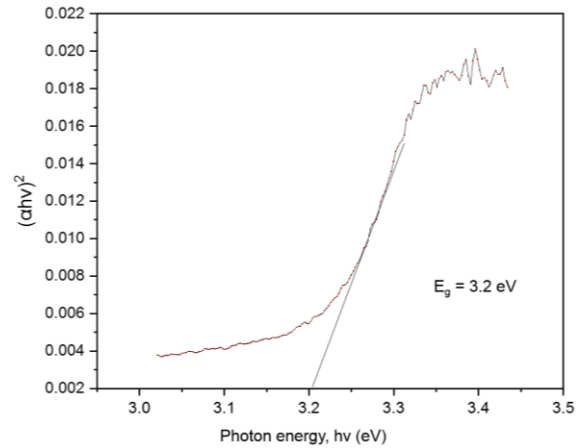


Fig. (4) Determination of energy band gap of as-prepared ZnO (0.1M) thin film before annealing

In Fig. (5), the gas sensitivity of ZnO films was measured after deposition at a concentration of 0.1M, with sensitivity plotted against temperature. The films were tested by exposing them to NO<sub>2</sub> gas. Unannealed films had lower sensitivity due to crystal defects and poor surface order, which hindered the interaction with NO<sub>2</sub> molecules. Films annealed at 450°C showed improved sensitivity due to reduced defects and increased crystallinity. The highest sensitivity was observed at 600°C, where annealing further reduced defects and increased crystallinity, creating more active sites for NO<sub>2</sub> adsorption and interaction. In summary, the gas sensitivity of the films to NO<sub>2</sub> increased as annealing increased crystallinity and reduced defects, which enhanced the electrical interaction and made them more effective in gas sensing applications.

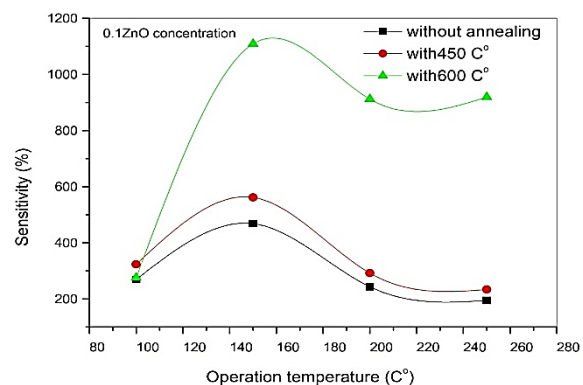


Fig. (5) Variation of sensing with operation temperature of 0.1M ZnO thin films before and after annealing at two different temperatures

Gas sensors performance is fundamentally governed by response time and recovery time as depicted in figures (6-8). Response time indicates the

speed at which the sensor responds to changes in the amount of gas, and recovery time measures how long it takes for the sensor to return to its original state after exposure to gas. These factors require optimization for adequate gas sensing. This clearly indicates the success of thin film in detecting gas concentration (0.1M) as can be observed when respectively comparing the spectra from figures. The graph for ZnO 0.1 films before annealing indicates very fast response and relaxation time of the gas, showing absolute sensitivity without annealing.

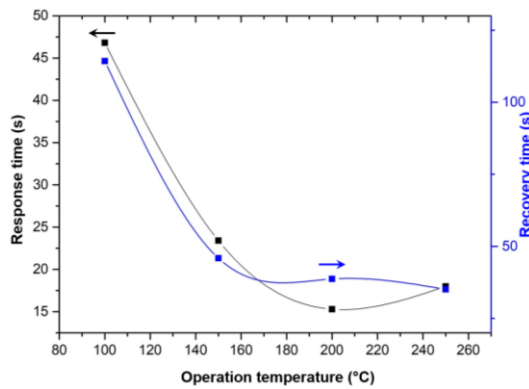


Fig. (6) Response and recovery times of 0.1M ZnO thin film before annealing

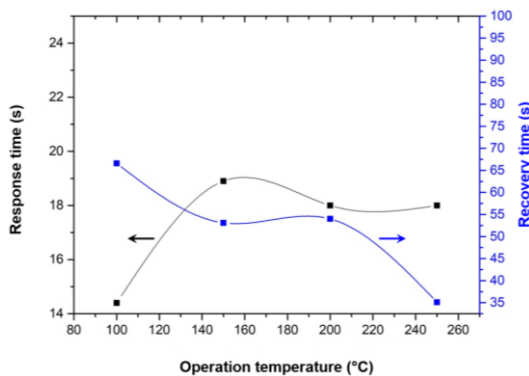


Fig. (6) Response and recovery times of 0.1M ZnO thin film after annealing at 450°C

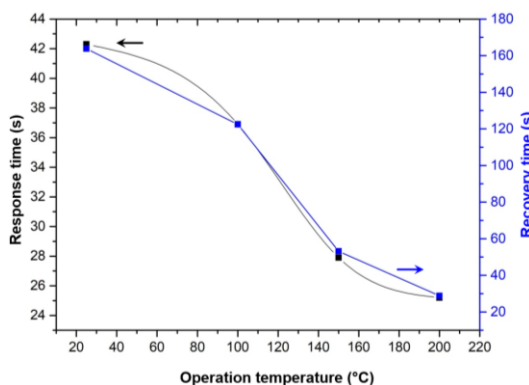


Fig. (6) Response and recovery times of 0.1M ZnO thin film after annealing at 600°C

#### 4. Conclusions

Based on the results of this study, it can be concluded that high-temperature annealing improves ZnO films' properties, such as grain size and uniform surface distribution, enhancing their optical and photophysical behavior. Increasing the annealing temperature also leads to a widening of the energy gap, affecting the films' optical properties. Furthermore, the sensitivity of the NO<sub>2</sub> gas sensor increases with annealing temperature and grain size, highlighting the importance of temperature control for achieving optimal gas sensor performance.

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