

RESEARCH PAPER

The Effect of Doping ZnO with Ni on the Films Composition and Its Sensitivity to NO₂ Gas

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ABSTRACT

In this study, nanocomposite Ni-doped ZnO thin films were successfully synthesized on glass substrates using the chemical spray pyrolysis (CSP) technique at a substrate temperature of 500 °C. The films had a thickness of approximately 300 nm and were doped at various ratios of Ni (0, 3.5, 5.5, 7.5, and 9.5%). An X-ray diffraction (XRD) study revealed that the nanostructures of all the deposited films (pure ZnO and nickel-doped ZnO) exhibit a hexagonal wurtzite structure, and that the preferred growth direction for all the deposited films is along the (002) plane, with no impurity phases observed in the Ni-doped ZnO samples. The results of the UV-visible spectral band gaps for the nanostructures of ZnO doped with Ni at different concentrations indicate a variation with changing Ni concentrations. Energy gaps of (3.35, 3.32, 3.3, 2.28 and 2.25) eV were obtained for the nanostructures containing Ni doping levels of (0, 3.5, 5.5, 7.5 and 9.5) % respectively. Gas sensing measurements towards hydrogen sulfide (NO₂) gas showed a significant enhancement in response for the 7.5.% Ni-doped film at an optimal operating temperature of 200 °C, the performance of the fabricated sensors in detecting NO₂ gas was tested at different operating temperatures (150-200 and 250°C) and concentrations (50–100 ppm). the highest response (221%) was obtained for the 7.5 % Ni-doped thin films when exposed to 100 ppm NO₂ gas, and the results were reproducible.

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INTRODUCTION

The research and development of gas sensors has become essential due to climate change caused by greenhouse gas emissions. Extensive studies have been carried out to develop gas sensors that combine high-performance materials with cost-effective manufacturing processes, whilst ensuring the sensors are compact and operate with sustained accuracy. It is well known that the properties of materials vary depending on crystal size and thin-film thickness.

Consequently, nanomaterials have ushered in a new era for numerous applications, including chemiluminescent cells, the manufacture of gas sensors and many other applications. It is likely that the structural, electrical and gas-absorption properties of gas sensors are determined by quantum size effects, which are beneficial for a variety of applications [1,2]. The efficiency of the sensors depends on their ability to capture gas molecules, their structure, and the properties of the materials used in the fabrication of the

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electrodes. Due to their unusual electrical, physical, chemical, and magnetic properties, nanometer-sized materials have recently received a lot of attention. The behavior of these materials differs from that of bulk semiconductors. As particle size reduces, the semiconductor's band structure changes. The bands' borders divide into discrete energy levels when the band gap increases. Quantum size effects are what they're called. These quantum scale effects have attracted a lot of interest in both basic and applied research [3,4]. Zinc oxide (ZnO) is a prominent semiconductor material characterized by a wide direct bandgap of ~3.37 eV and a large exciton binding energy of 60 meV at room temperature. Doping ZnO with transition metal ions, particularly Nickel (Ni²⁺), is an effective strategy to tailor its electronic structure, optical bandgap, and catalytic surface properties without altering the hexagonal wurtzite network. Due to the proximity of the ionic radius of Ni²⁺ (0.69 Å) to that of Zn²⁺ (0.74 Å), nickel ions readily substitute zinc ions within the lattice matrix. Among various synthesis avenues, the Chemical Spray Pyrolysis (CSP) technique stands out due to its simplicity, cost-effectiveness, high deposition rate, and capability to produce uniform, large area thin films. In Ni-doped ZnO thin films essential inorganic semiconductors that could be used in Li-ion batteries, gas sensors, chemical catalysts, and magnetic storage systems. [5,6]. Their composites also drew a lot of interest because of their stability, excellent gas-sensitive features, and prospective

use in Li-ion battery electrodes [7-9]. this study, Ni-doped ZnO thin films were synthesized using ZnCl₂ and NiCl₂ precursor salts aims to fabricate ZnO films doped with varying proportions of nickel and investigate how this doping affects structural properties using X-ray diffraction (XRD) and optical properties using visible and ultraviolet spectroscopy (UV-Vis). Performance in target applications, such as gas sensing, will also be evaluated. The optical constants, and NO₂ gas sensing characteristics as a function of Ni doping concentration are comprehensively reported and discussed.

MATERIALS AND METHODS

Ni-doped ZnO were synthesized by a chemical spray method. first: mixture of 0.1 mol ZnCl₂ 6H₂O which was dissolved in 100 ml distilled water was stirred for 30 min at 50 °C. second: mixture of 0.1 mol NiCl₂ 6H₂O which was dissolved in 100 ml distilled water was stirred for 30 min at 50 °C. Then 0, 3.5, 5.5, 7.5 and 9.5 mmol of NiCl₂ 6H₂O nickel Chloride hexahydrate were doped to first solution, respectively. After being stirred for another 30 min and obtained solution was transferred to a spray pyrolysis, and sealed and heated up to 500 °C. The use of dry air as the carrier gas ensured the efficient transportation of precursor solutions into the nebulizer, while also supplying the necessary pressure for the atomization of these solutions. The thickness of the samples was calculated using the following equation [10]:

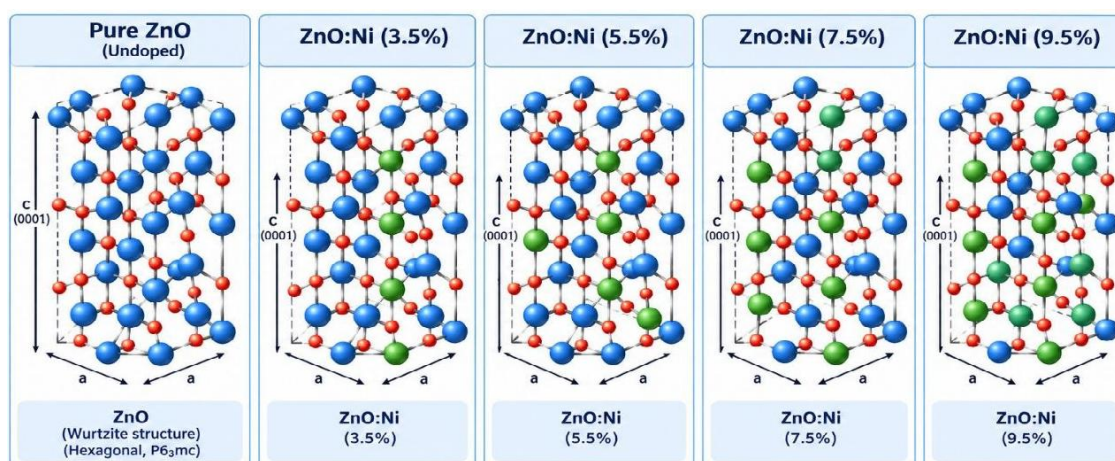


Fig. 1. Crystal structure of Ni-doped ZnO (Ni concentrations: 0, 3.5, 5.5, 7.5 and 9.5 %).

$$t = \Delta m / A \cdot \rho \quad (1)$$

't' the thickness of the thin films, the change in mass, denoted by the symbol ' Δm ', is a fundamental concept in physics. ρ is the density of the thin-film material, the thickness of which was measured as 300 nm. after the samples had been prepared, their structural properties were studied by using X-ray diffractometer (Bruker D₂ phaser, filtered Cu K α , Japan), wherein the scanning angle (2θ) range from (20° to 80°). The optical properties of all thin films sample were examined using UV–Vis-NIR spectrophotometer ((Perkin Elmer, Lambda 25, USA) in range from 190 nm to 1100 nm. The gas-sensing performance of nanostructures made from zinc oxide (ZnO) and doped by Ni was investigated using a gas sensor specifically developed for this purpose. All the sensors were tested to verify their ability to chemically detect

gases using solid-state technology. The thin films were coated with silver paste electrical contacts, spaced 1 cm apart. All the sensors were installed in the 250 cm³ test chamber, which is made of a rust-resistant material (steel), fitted with an inlet (for introducing the test gas) and an outlet (for removing the test gas or introducing fresh air). The required amount of test gas was introduced into the chamber by injecting an appropriate quantity of nitrogen dioxide (NO₂) using a micro-syringe. The response of the sensors to nitrogen dioxide (NO₂) was calculated using the following equation [11-14].

$$S = ((R_g - R_a) / R_a) \times 100\% \quad (2)$$

where $((R_g - R_a) / R_a) \times 100$ is the percentage change in resistance representing the sensitivity to NO₂ gas.

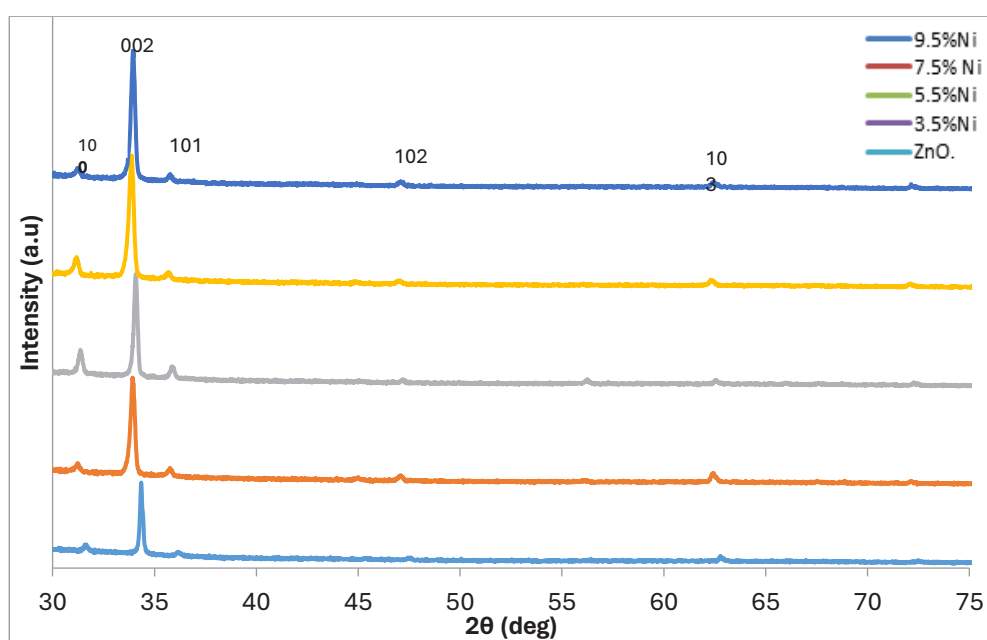


Fig. 2. XRD patterns of Ni-doped ZnO (Ni concentrations: 0, 3.5, 5.5, 7.5 and 9.5 %).

Table 1. Shows that the crystal size of all samples.

Ni content (at.%)	2θ (deg) (002)	Crystallite Size [nm]
ZnO pure	33.8268	34.6
3.5 Ni	33.896	40.7
5.5 Ni	34.0465	57.9
7.5 Ni	34.3309	106.2
9.5 Ni	34.0752	35.1

RESULTS AND DISCUSSION

Crystal structure

Fig. 1. Here is what actually happens: a schematic representation of the crystal structure of pure ZnO of the hexagonal 'wurtzite' type, and ZnO doped with Ni at various Ni concentrations (0, 3.5, 5.5, 7.5 and 9.5 %). The zinc, oxygen and nickel atoms are represented by blue, red and green spheres, respectively. It is assumed that the nickel atoms replace the zinc atoms in the crystal lattice

of the ZnO [15-16].

Structural Analysis (XRD)

XRD patterns of pure and Ni-doped ZnO nanostructures are presented in Fig. 2. All samples exhibit diffraction peaks corresponding to the (100), (002), (101), (102) and (101) planes, which unequivocally indicate the standard hexagonal wurtzite phase of ZnO. The preferential growth orientation is observed along the c-axis (002)

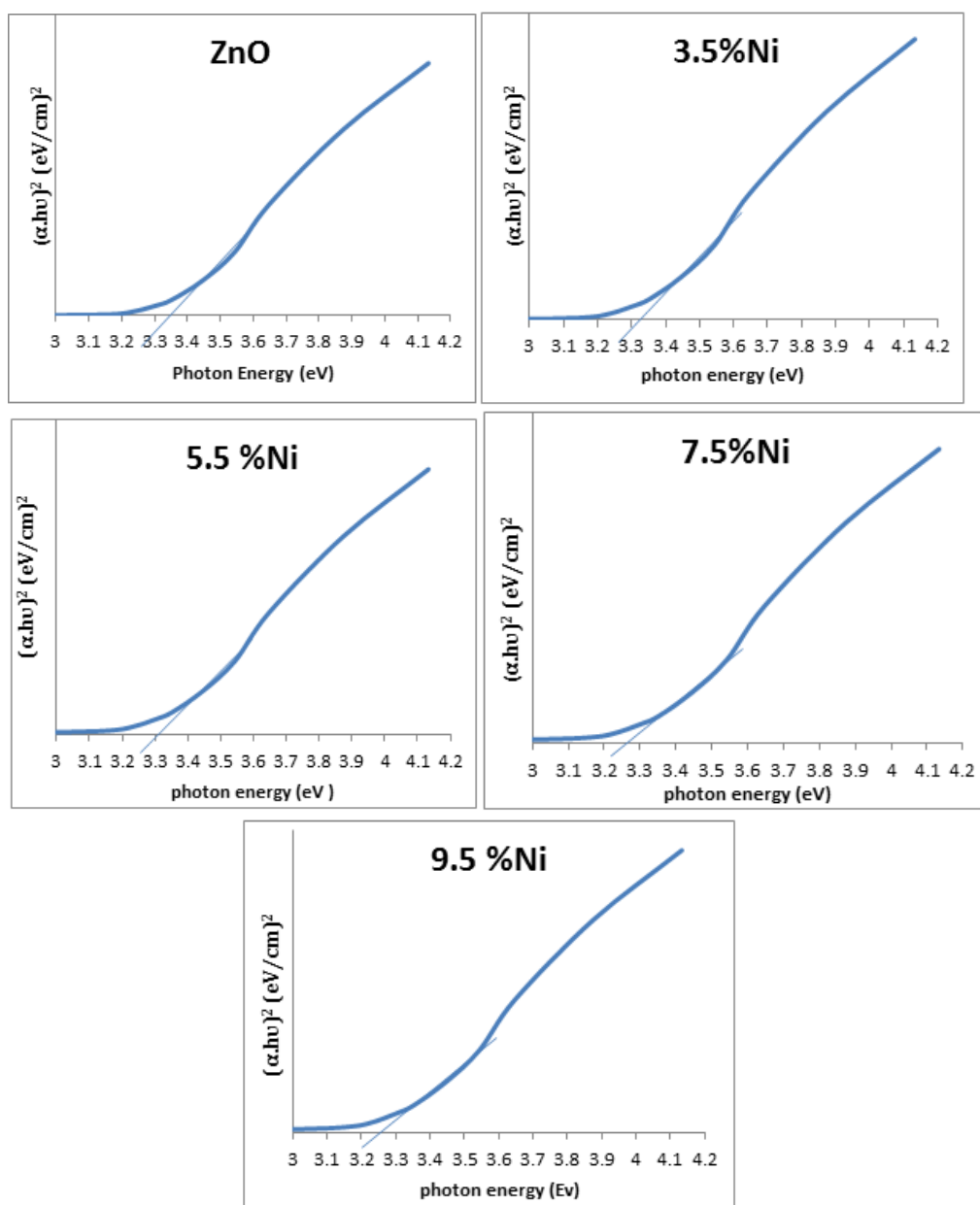


Fig. 3. Band gap variation in Nano thin film productions at 0, 3.5, 5.5, 7.5 and 9.5 % of Ni doping.

axis. Upon the addition of Ni a slight shift of all peaks towards bigger angles (2θ) is noted, this is attributed to the substitution of larger Zn²⁺ ions with the smaller Ni²⁺ ions [17].

From the figure above (Fig. 2), the strongest peak intensity in the x-ray diffraction analysis indicated that the preferred growth direction was the (002) plane, indicating the formation of nanolayers in the structure of samples [18]. The estimation of the mean nanocrystal size was derived from the

Scherrer relation [19]. The following equation is used to calculate the result:

$$D = (0.9\lambda) / (\beta \cos \theta) \quad (3)$$

In this study, the average nanocrystal size (D) is considered, along with the wavelength of the X-ray utilized (λ), the cosine of the Bragg angle ($\cos \theta$), and the full width at half maximum (β). The Scherrer constant, denoted by K , is a pivotal

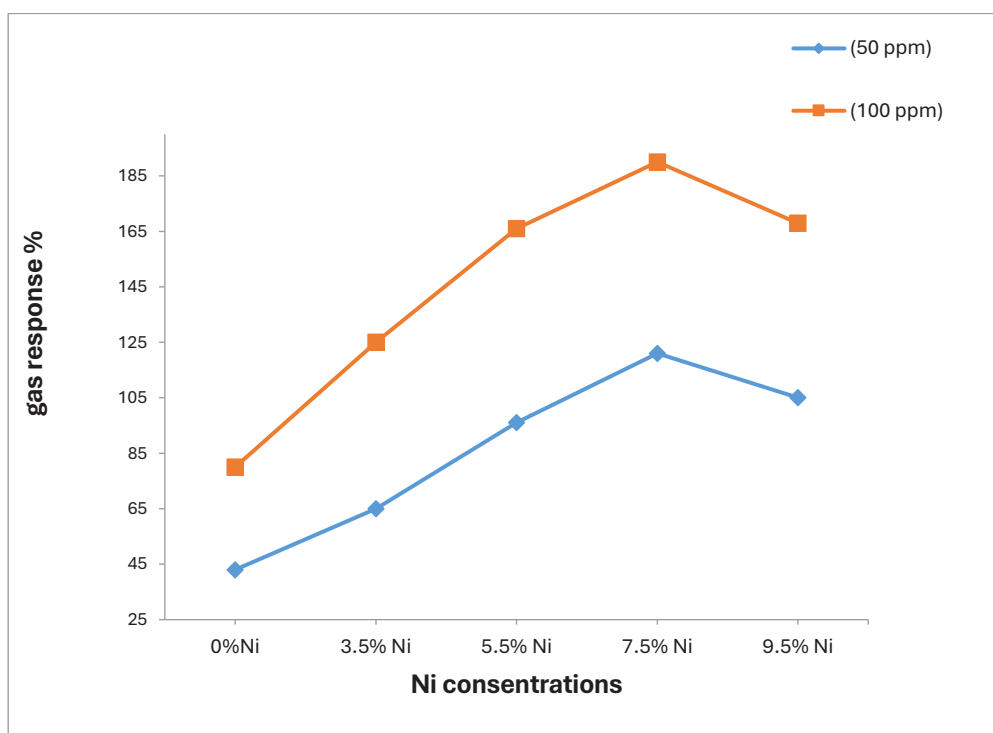


Fig. 4. response of a ZnO/Ni sensor to two different concentrations of NO₂ gas at an operating temperature of 200 °C.

Table 2. The values of band gap for all samples.

Ni content (at.%)	Band gap energy (eV)
ZnO Pure.	3.35
3.5 Ni	3.32
5.5 Ni	3.3
7.5 Ni	3.28
9.5 Ni	3.25

parameter in this analysis, with a value of 0.9 being employed.

Table 1. shows that the crystal size increased systematically from 34.6 nm to 35.1 nm with increasing Ni doping concentration. This reduction indicates that Ni^{2+} ions act as grain growth inhibitors.

UV–Visible analysis

Fig .3. displays the plot of $(\alpha \cdot hu)^2$ (eV/cm^2) against photon energy for both pure ZnO and ZnO doped with Ni at concentrations of (3.5 ,5.5 ,7.5 ,9.5 %). the intersection point has been identified by plotting the additional straight-line part on the x-axis (the optical band gap). The optical energy gap (E_g) was determined by Tauc equation as given below, [10]

$$\alpha hu = B[hu - E_g]^n \quad (4)$$

It can be assumed that (B) is Tauc constant, (hu) is the energy of the photon, and (α) is the absorption coefficient.

Table 2 shows that the band gap of all thin films is in the range (3.35 eV-3.25 eV) as the Ni doping concentration increases. This decreases in the is

ascribed to sp-d mixing interactions between the band electrons in the ZnO host lattice and the valence electrons of the Ni substituted atoms [20].

Gas-sensing performance

The gas sensing capability for both pure ZnO and ZnO doped with Ni at concentrations of (3.5 ,5.5 ,7.5 ,9.5 %) was tested against 50 ppm and 100 ppm of target gas (NO_2) at operating temperatures ranging from 200 °C. From fig.4. We can see that the addition of Ni to ZnO significantly increased the gas response. The response of NO_2 gas show increases whenever concentration of gas increases from 50ppm to 100 ppm. The response increased from 43 in the ZnO pure to 65 at a doping level of 3.5 % Ni, and then to approximately 96 at a doping level of 5.5 % Ni in 50 ppm, and the response increased from 80 in the ZnO pure to 125 at a doping level of 3.5 % Ni, and then to 166 at a doping level of 5.5 % Ni in 100 ppm. The reason for this increase is the Increase in the number of active sites, as doping causes more defects and active sites on the surface of the material. These sites facilitate the adsorption of gas molecules (such as laboratory gas) and their reaction with oxygen, which increases the change in electrical

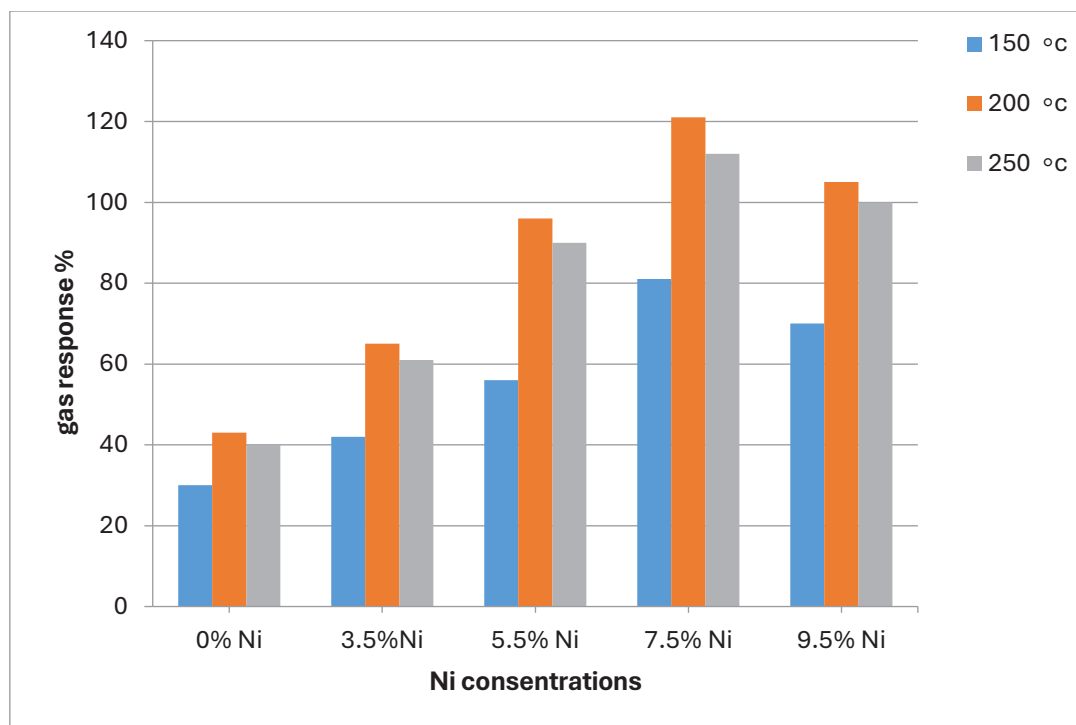


Fig. 5. Gas-sensing response of ZnO/Ni sensors towards 100 ppm NO_2 gas at 150, 200, 250 °C operating Ni concentrations.

resistance and consequently raises the response gas [21].

In Fig. 5. the observed result indicates that the sensor containing 7.5% Ni at an operating temperature of 200 °C will exhibit the highest response of the gas (121%) compared with the other sensors. It is noted that for all sensors at operating temperatures below 200 °C, the sensor response is low due to insufficient energy being available to adsorb NO₂ gas onto the film surface; conversely, at temperatures above 200 °C, the response is determined by the diffusion rate of gas molecules. thus, at 200°C, these two processes balance out, and the sensor exhibits its highest response of 7.5% Ni [22].

CONCLUSION

We used chemical spray pyrolysis to create ZnO thin films with different Ni concentrations (0, 3.5, 5.5, 7.5, and 9.5%) on a glass substrate at 500°C. A study using X-ray diffraction (XRD) revealed that the nanostructures of all the deposited films (pure ZnO and Ni-doped ZnO) exhibit a hexagonal wurtzite structure, and that the preferred growth direction for all the deposited films is along the (002) plane, with no impurity phases present in the Ni-doped ZnO samples. according to their optical properties, when Ni concentrations increase, the band gap decreases, ranging from 3.35 eV to 3.25 eV. We tested the performance of the manufactured sensors for their ability to detect nitrogen dioxide (NO₂) at various operating temperatures and gas concentrations. The highest response (221 %) was obtained with thin films doped with 7.5 % nickel when exposed to 100 ppm of NO₂ at 200 °C.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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