



Emphasis on the importance of Ga-doped ZnO thin film gas sensors fabricated by the SILAR approach for ammonia detection

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ABSTRACT

This study highlights the importance of ZnO-based thin film sensors in gas-sensing applications and examines the impact of gallium concentration on their ability to detect ammonia. Ga-doped ZnO thin films were fabricated using the successive ionic layer adsorption and reaction (SILAR) method with varying doping concentrations. A series of samples was prepared, ranging from pure ZnO to films doped with 2%, 4%, 6%, and 8% Ga. The structural, morphological, and optical characteristics of the synthesized ZnO sensors were examined using various physical and chemical characterization techniques. XRD analysis confirmed that increasing the Ga doping concentration enhanced the degree of crystallization within the ZnO lattice. As the lattice parameter c increased, a corresponding decrease in the (002) diffraction intensity was observed, accompanied by a slight shift of the diffraction peaks toward lower angles. SEM observations revealed that the incorporation of Ga significantly influenced both the size and morphology of the ZnO nanostructures, likely due to its role in nucleation and crystal growth processes. Notably, a morphological transition from nanoflower-like structures to hexagonal nanodiscs was detected as the Ga doping concentration increased. Raman spectroscopy further verified the successful incorporation of Ga ions into the ZnO lattice through the observed shifts in the $E_2(\text{high})$ phonon mode. The phonon mode at 439 cm^{-1} , characteristic of pure ZnO, exhibited a redshift with increasing Ga content. FTIR spectra displayed distinct peaks in the low-wavenumber region ($400\text{--}800\text{ cm}^{-1}$), corresponding to Ga–O and Zn–O vibrations, indicative of metal–oxygen bonding. With increasing Ga incorporation, minor variations in peak intensity and position were observed, confirming the substitution of Zn atoms by Ga within the lattice. Gas sensing measurements demonstrated that the fabricated films exhibited high sensitivity toward ammonia (NH_3) gas at room temperature. The improved response was attributed to both the morphological evolution and the electronic contribution of Ga dopants. Notably,

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the 6GZO sensor achieved a maximum response of 198% to 100 ppm NH_3 at 25 °C, along with fast response and recovery times of 7 and 8 s, respectively, and excellent selectivity compared to other target gases.

1 Introduction

Sensors are embedded in many modern technologies, including smartphones, vehicles, and home automation systems, where their ability to collect environmental data and adjust device behaviour accordingly enhances operational efficiency [1]. Among them, gas sensors are compact devices designed to detect gas leaks and transmit an alarm signal to the control unit, which plays a crucial role across a wide range of fields, contributing significantly to safety, environmental protection, and overall quality of life [2].

Thin-film sensors are widely utilized in various applications, including environmental monitoring, medical diagnostics, and industrial process control. Their relatively low fabrication cost enables large-scale manufacturing through high-volume production techniques [3]. Additionally, their small size and low mass often make them more advantageous than other types of sensors. Metal oxide semiconductors (MOS), also known as valence compounds, exhibit strong ionic interactions between metal cations and oxygen anions. Their intrinsic defects and oxygen vacancies facilitate the adsorption of gas molecules on the surface, enabling the fundamental gas-sensing reaction. Commonly used metal oxides in gas sensors include zinc oxide (ZnO), tin oxide (SnO_2), tungsten oxide (WO_3), titanium dioxide (TiO_2), and indium oxide (In_2O_3). The primary advantages of MOS-based gas sensors include their low-cost, high sensitivity, stability, and tunable surface morphology [4].

In metal-oxide semiconductors, the interaction between metal and oxygen orbitals significantly influences the charge carrier transport by modifying the energy transfer pathways. These interactions—and the resulting electronic properties—depend on factors such as the type of metal and oxide, crystal structure, and the concentration of defects or impurities. Such modifications are critical for applications in electronic devices, catalysis, and gas sensing [5]. In n-type MOS materials, electrons possess a lower

effective mass compared to holes, which enables more efficient electron transport and enhances electrical conductivity. Owing to their high sensitivity, fast response and recovery times, and reliable detection of various volatile and hazardous organic compounds, MOS gas sensors are widely preferred for gas-sensing applications [5]. Modifying the morphology, dimensions, and composition, as well as the directional synthesis of micro and nanostructures, is essential for advancing gas sensor research [6–8]. Materials possessing unique structures have demonstrated significant potential in fields such as sensors, catalysis, and energy storage [9–11]. Over the past decade, self-assembled micro- and nanomaterials exhibiting distinctive features have garnered significant interest from researchers [12, 13].

In gas sensing, sensors utilizing self-assembled micro and nanomaterials are extensively employed for detecting flammable, explosive, and poisonous gases [14]. Particularly in research concerning morphological alterations, enhancements in gas sensor sensitivity, and reductions in operating temperature are noted. The literature indicates that morphological changes occur with varying doping rates in the conducted experiments [15]. Recently, Ga has been a very popular dopant element in ZnO thin films. This is mainly because the ionic and covalent diameter of the element Ga (ionic: 0.62 Å; covalent: 1.26 Å) is smaller and closer than Zn (ionic: 0.74 Å; covalent: 1.31 Å) [16]. Since Ga^{3+} ions have a smaller ionic radius compared to Zn^{2+} ions, their substitution into the ZnO lattice causes lattice shrinkage and the resulting lattice distortion. This leads to an increase in crystal defects, changes in growth orientations, and a noticeable alteration in grain morphology (such as nanorods, nanoplates, or granular structures) [17]. Moreover, the charge imbalance introduced by Ga doping enhances the growth rate of certain crystal planes—particularly the (002) plane—while suppressing growth in other directions. As a result, grains may form in denser, smaller, or more

loosely packed structures, which can lead to the transformation of ZnO from its typical nanoflower morphology into more compact nanostructures [18].

Analysis of literature reveals that the morphology of the samples is altered by Ga doping [19–22]. Reports indicate that alterations in morphology result in observable enhancements in gas sensor sensitivity. Xavier and Swati have investigated Ga-doped WO_3 thin films via the spray pyrolysis process for acetaldehyde gas-sensing applications. Various doping ratios (from 0.025 to 0.1 Ga doping ratios) were fabricated, and SEM analyses revealed morphological alterations in the sensors contingent upon the doping levels, with a comprehensive examination of gas sensor studies conducted. A sensitivity of 98.09 was achieved at room temperature for the sample with a 0.1 Ga doping ratio in response to acetaldehyde gas [19].

Patil et al. have reported that gallium (Ga)-doped ZnO (GZO) nanorods (with 1, 2, 3, 4, and 5% Ga doping) synthesized through the reflux process were examined. Increasing the concentration of 'Ga' results in changes to the shape of GZO thin films [19]. At reduced 'Ga' concentrations in the ZnO matrix, the nanorods exhibited a slanted orientation and a diameter of 200 nm. With a modest elevation in the 'Ga' doping concentration, the randomly inclined nanorods achieve vertical alignment. Furthermore, the diameter of the rods continues to increase, reaching 250 nm, and their surfaces assume a hexagonal configuration. Secondary growth on the surface of the nanorods is detected with a doping concentration of around 3% Ga, resulting in surface damage to the nanorods. Furthermore, the diameter of the nanorods, namely 100 nm, diminishes while the density of the nanorods grows with a further rise in 'Ga' concentration. This offers more adsorption sites for gas molecules. The decrease in gas sensitivity at GZO-5 may be due to the reaction of 'Zn' and 'Ga' to the formation of the second phase of alloyed compounds. The transit graph of GZO thin films at different gas concentrations, ranging from 10 to 100 ppm, at 175 °C. It can be seen that the GZO thin films detect low-level detection of NO_2 gas up to 10 ppm. [19].

Thirunavukkarasu and Jothiramalingam [21] have synthesized Ga-ZnO nanodisks and nanorods using a polymer-assisted hydrothermal process. The creation of low-concentration routes leads to the formation of thin films with reduced thickness, as aggregated seed particles hinder the complete development of nanodisk formation in the polymer-assisted hydrothermal

process, whereas accelerated growth of nanorods is achieved from ZnO seed particles. The adjusted concentration of Ga-ZnO (0.5) sol-gel solution results in increased film thickness and larger crystallite size during the annealing process [21]. The form of nanodisks is solely determined by the interaction of polymer molecules with the surface layers of Ga-ZnO seed particles during the hydrothermal process. The diverse heights of nanorod/nanodisk development were achieved with 1% Ga-ZnO (0.2), comparable in size to ZnO nanorods synthesized by traditional methods. The influence of polymer content and duration of hydrothermal treatment on the development of 1% Ga-ZnO (0.5) nanodisks on an AlN substrate has been investigated. An increase in polymer concentration (from 4 to 8% polymer concentration) during the hydrothermal process results in a more slender nanodisk morphology compared to the sample produced at a lower polymer concentration. Polymer concentrations of 3% and 4% yield a refined nanodisk shape. Elevated polymer concentration (4%) leads to the production of quality nanodisk. The higher UV-light sensing activity and faster recovery time were achieved for 1% Ga-ZnO (0.5) and 1% Ga-ZnO (0.2) on an AlN substrate compared to the conventionally prepared Ga-ZnO thin film [21].

Ungula et al. synthesized Ga/Zn sol-gel solutions by adjusting the pH values of the Ga/Zn solution to 3, 5, and 8. The SEM images of the resulting samples were then analyzed [22]. Under acidic conditions (pH 3), microscopic clustered rods appeared on extensive nanorod sheets, whereas larger and comparatively dispersed nanospherical particles were observed at pH 5. At pH 8, larger and well-dispersed nanospherical particles composed of aggregated nanocrystallites were discovered, as evidenced by the surrounding particles. Instances of robust clustering of nano-grains are observable at pH 8, as evidenced by the formation of nanospherical structures. Upon elevating the pH to alkaline levels (pH 8), it was anticipated that clustered GZO nanoparticles would exhibit reduced surface roughness and a uniform nanostructure. The enhancement in grain size clearly indicates the extent to which the nanoparticles are influenced by the pH of the precursor solution [22].

Various methodologies for fabricating Ga-doped ZnO nanostructures and their corresponding characteristics have been investigated. These approaches employed intricate processes involving extremely high temperatures or pressures and incurred significant

costs [23–25]. The SILAR method offers numerous advantages over alternative synthesis techniques, including low temperature, atmospheric pressure, ease of control, simplicity, non-toxicity, high yield, environmental friendliness, and cost-effectiveness [26, 27]. Moreover, the SILAR method is highly versatile in terms of altering several parameters, including temperature and reactant concentration, which can influence the form, size, and morphology of the nanostructures.

Research on ammonia gas sensors that can be produced at low-cost and operate at room-temperature remains important. In this work, different doping ratios were used for Ga-doped ZnO thin films, and their NH_3 gas-sensing properties were investigated. From a practical perspective, the ammonia gas sensor operating at room temperature is designed to be sensitive under ambient conditions due to its low power consumption and ease of use. Results from Ga-doped ZnO gas sensors produced by the SILAR method showed very high sensitivity to ammonia gas at room temperature. Also, the produced samples have very fast response and recovery times. Therefore, they have great potential for producing gas sensors that can be used in daily applications.

2 Experimental

One of the newest solution techniques for forming thin films is the SILAR technique. SILAR is an aqueous solution technique involving sequential reactions at the substrate-solution interface [28]. It is a simple technique that allows thin films to be formed by immersing the substrate in a specific sequence of aqueous solutions containing ions of each species and precipitating them onto the substrate. Since the reaction is carried out at or around room temperature and under pressure enveloping the solutions, various base materials, such as insulators, semiconductors, metals, and temperature-sensitive materials (like polyester), can be used. As it is a low-temperature process, oxidation and corrosion of the base material are also prevented. The key to obtaining high-quality thin films with the SILAR technique is to carefully regulate the preparation conditions, including precursor concentration, counterion type, pH, precursor solution adsorption, reaction time, and rinsing time [29].

Before deposition, glass substrates were meticulously cleaned using detergent, deionized water,

ethanol, and acetone, followed by air drying. The SILAR procedure involved sequential immersion in cationic and anionic precursor solutions to construct a ZnO layer incrementally. Zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ served as the source of Zn^{2+} ions in the cationic solution. The anionic solution of ammonia (NH_4OH) supplies OH^- ions for the synthesis of zinc hydroxide. Throughout each SILAR cycle, the substrate was submerged in the cationic solution to facilitate the adsorption of Zn^{2+} ions onto its surface. Following a rinse in deionized water to remove excess ions, the substrate was immersed in the anionic solution, resulting in the formation of $\text{Zn}(\text{OH})_2$ through a surface interaction between Zn^{2+} and OH^- ions. The glass substrate is removed from the solution and kept in distilled water at 90°C for 7 s. The aim here is to provide $\text{Zn}(\text{OH})_2 \rightarrow \text{ZnO}$ conversion. The glass base material is removed from distilled water at 90°C and dried in air for 60 s. Finally, the glass substrate is rinsed in distilled water at room temperature for 30 s. Pure ZnO was grown for 20 cycles.

After that, Zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and gallium nitrate $[\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}]$ served as sources of Zn^{2+} and Ga^{3+} ions in the cationic solution. The anionic solution comprised ammonia (NH_4OH) to supply OH^- ions. In each SILAR cycle, the substrate was initially immersed in the cationic solution, facilitating the adsorption of Zn^{2+} and Ga^{3+} ions onto its surface. Following a brief rinse in deionized water to remove loosely attached ions, the substrate was submerged in the anionic solution, resulting in a chemical interaction between the adsorbed metal cations and hydroxide ions that facilitated the creation of a thin layer of Ga-doped $\text{Zn}(\text{OH})_2$. The sequence was performed for a specified number of cycles to attain the appropriate film thickness. Samples were grown for 20 cycles. The deposited films were subsequently rinsed, dried, and annealed at 300°C in air for 15 min in an annealing furnace, hence improving the

Table 1 Renaming of produced thin films

Names of produced Thin films	Renamed
Pure ZnO	ZnO
2% Ga-doped ZnO	2GZO
4% Ga-doped ZnO	4GZO
6% Ga-doped ZnO	6GZO
8% Ga-doped ZnO	8GZO

film's structural and electrical characteristics. The codes for the samples are listed in Table 1.

A computer-controlled gas detection system developed in our laboratory was used to evaluate the NH_3 gas detection performance of each sample. The system utilized MKS mass flow controllers (MFCs) to regulate and determine the mixing ratios of the sweep gas and the target gas. A LakeShore 325 temperature controller was used to monitor and control the sample temperature, and the system maintained a stable temperature at ambient conditions. A Keithley 2400 SourceMeter was employed for current measurements. The setup also included a vacuum pump to purge the sensor chamber and prevent the release of uncontrolled gas. Dry air served as the sweep gas throughout the experiments.

Electrical measurements were performed by applying interdigitated (IDT) electrodes on the sample surface using silver paste. Current–voltage (I–V) curves were recorded prior to gas exposure to verify the quality of the IDT contacts and electrical connections. The resistance values of the samples at room temperature were calculated from these I–V curves. After confirming proper contact, the samples were placed in the sensor cell and connected to the measurement system. Following the I–V tests, ohmic contact was established, the connections were rechecked, and NH_3 gas-sensing measurements were initiated. Gas detection measurements were carried out at room temperature for NH_3 concentrations of 25, 50, 75, and 100 ppm. Before each measurement, dry air was passed over the samples for 30 min to ensure baseline stability. Subsequently, the target gas was introduced into the chamber while maintaining a constant flow of air. This stabilization period enabled the system to reach thermal equilibrium, thereby minimizing measurement errors caused by temperature fluctuations. During testing, the relative humidity (RH) of the indoor environment was approximately 35%.

3 Results and discussion

Figure 1 presents the XRD patterns of the synthesized samples. All films exhibited a polycrystalline nature, with diffraction peaks corresponding exclusively to the zincite phase of ZnO, indicating successful crystallization without any secondary phases. The characteristic diffraction peaks were identified at the (100), (002), and (101) planes, consistent with the standard

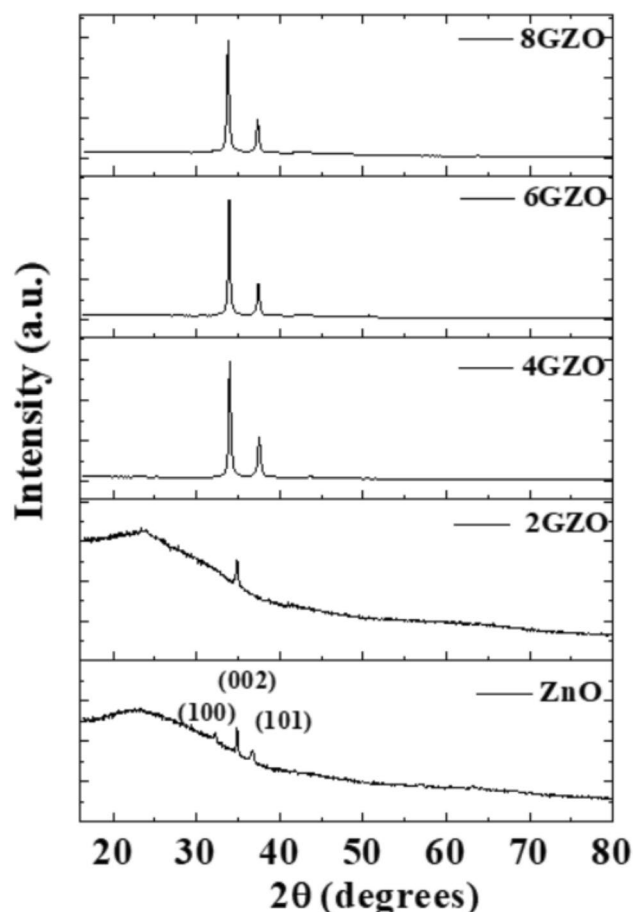


Fig. 1 XRD spectra of pure and doped ZnO thin films

JCPDS card No. 36-1451 [30]. With increasing dopant concentration, the intensity of the (002) diffraction peak showed a general enhancement, whereas the intensity of the (101) peak tended to decrease, suggesting a preferred orientation along the c-axis.

Furthermore, no additional diffraction peaks corresponding to Ga-related oxides or possible Ga–Zn binary phases were detected within the XRD spectra, confirming that Ga atoms were successfully incorporated into the ZnO lattice as substitutional dopants without disrupting the crystalline integrity of the host matrix. This behavior can be explained by the difference in the ionic radii of Zn^{2+} (0.74 Å) and Ga^{3+} (0.61 Å) [31]. Since the ionic radius of Ga^{3+} is smaller than that of Zn^{2+} , increasing the Ga doping concentration does not promote crystal growth; instead, it maintains the lattice structure of ZnO, allowing Ga atoms to be smoothly integrated into the wurtzite framework.

The uniformity of the patterns confirmed the wurtzite structure of ZnO in the presence of Ga

doping. The peak position shift due to Ga doping occurs at lower angles, indicating successful incorporation of Ga^{3+} ions into the ZnO host structure [31]. The absence of supplementary peaks indicates that the chosen synthetic process effectively inhibited the formation of secondary phases, including pure gallium metal, gallium oxides (Ga_2O_3), and binary zinc gallium oxides (ZnGa_2O_4).

When Ga with 2 at% is added to ZnO, the preferential plane (101) intensity is decreased, which shows the crystallinity degradation that may be due to the sudden incorporation of Ga in the ZnO matrix. The addition of Ga with 4 at% increases the intensity, which may be due to the proper incorporation of Ga in the ZnO matrix. Moreover, the Ga ions occupy the Zn lattice in the ZnO matrix properly, resulting in an increase in intensity. It is seen that the sharpening of the crystal peaks increases with the increase in the density of additive atoms. Obviously, for 4GZO, 6GZO, and 8GZO, the intensity of the (002) diffraction peak is much greater than that of the other samples, suggesting that these samples have the best crystallization among the other samples.

Upon examining the literature, an increase in the c orientation (002 direction) has been observed in many previously obtained ZnO films. On the other hand, Cheong et al. reported an increase in c-axis orientation was also observed in the study conducted by [32]. Amirhaghi suggested that this orientation is due to the growth of the films in this direction, resulting from the high atomic density in the (002) plane [33]. Bao explained the reason for the orientation in terms of decreasing internal tension and surface energy [34].

Yoshino et al. They reached a similar result in their study, and as a result, they stated that well-crystallized ZnO films can be obtained using the III-A group elements as additives [35]. Reddy, in his study (2002), observed an increase in the XRD peaks of the plane with an increase in the heat treatment temperature and attributed it to improved crystallization [36].

Fortunato et al. Peak intensities were obtained only in the (002) plane. While interpreting this situation, the author stated that all films are polycrystalline and hexagonal, and are arranged with the c-axis perpendicular to the base [37]. Hirata et al. reported that only two peaks were observed in the study conducted, and these peak intensities sharpened with increasing coating temperature. The author attributed this result to the increase in particle size [38].

In addition, when the most dominant peak (002) is examined, it is observed that a shift occurs due to doping. While the angle of the peak was 34.88 degrees for undoped ZnO and 2GZO samples, it was measured as 33.98, 33.94, and 33.79 degrees for 4GZO, 6GZO, and 8GZO, respectively. A shift towards smaller angle values was observed in the peak angle values. Farha et al. have reported that the position of XRD peaks of Ga-doped ZnO, compared to a pure ZnO sample, exhibits a visible shift in the position of XRD peaks to lower 2θ values with increasing Ga concentration [39]. The average crystallite sizes of the films were estimated from XRD using the given formula [40];

$$D = \frac{0.94\lambda}{\beta \cos \theta}, \quad (1)$$

where λ is the wavelength of x-ray radiation, θ is the full width at half maximum (FWHM), and is the diffraction angle. The Crystalline size of the samples was estimated to be 135, 51, 45, 38, and 42 nm for ZnO, 2GZO, 4GZO, 6GZO, and 8GZO, respectively. The lattice strain formula is shown by Eq. (2) below [41];

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (2)$$

Lattice strain of pure and doped ZnO samples was calculated as 0.0945, 0.2549, 0.2915, 0.3331, and 0.3090 for ZnO, 2GZO, 4GZO, 6GZO, and 8GZO, respectively. The lattice strain values measure the extent of distortion in the crystal structure of ZnO caused by internal stressors. The strain for the pure ZnO sample is minimal (0.0945). The introduction of gallium into the structure (2%, 4%, 6%, and 8% Ga-doped ZnO) dramatically increases lattice strain (to 0.2549, 0.2915, and 0.3331), demonstrating that Ga inclusion induces further distortion in the ZnO lattice. This distortion typically arises from Ga^{3+} ions substituting for Zn^{2+} ions, leading to changes in bond lengths and lattice properties. At 8% Ga doping, the strain marginally lowers to 0.3090, indicating potential lattice relaxation or that surplus Ga results in defect clustering instead of further substituting into the ZnO lattice. The dislocation density is a measure of the number of dislocations in a unit volume of a crystalline material. Dislocation density is calculated by Eq. (3) [42];

$$\delta = \frac{1}{D^2} \quad (3)$$

The dislocation density of pure and doped ZnO samples was calculated as 5.49×10^{-5} , 3.84×10^{-5} , 4.94×10^{-5} , 6.93×10^{-5} and $5.67 \times 10^{-5} \text{ nm}^{-2}$ for ZnO, 2GZO, 4GZO, 6GZO, and 8GZO, respectively. Similar structural changes have been observed for Ga doping in ZnO in the literature, showcasing no Ga peaks in the XRD pattern [40, 43, 44]. The increase or decrease of ϵ can induce an arrangement of atomic positions and increase the (002) preferred orientation in the lattice, thereby altering all the physical properties of the films. In the literature, the shifting of the (002) peak positions to higher or lower angles triggers a decrease or increase in the ϵ and δ values of the GZO thin films [42].

SEM analysis of the produced samples is given in Fig. 2. Upon examining SEM analyses, it is observed that there is a remarkable change in morphology depending on the Ga contribution ratio. It is observed that the nanoflower structures formed in the undoped ZnO structure transform into hexagonal nanodisc structures upon the introduction of Ga-doped atoms into the ZnO structure. It is quite remarkable that this change changes linearly with each contribution ratio. With 8% doping, the structure starts to deteriorate again. The introduction of impurity atoms can significantly affect the size and morphology of a crystal by influencing nucleation and growth mechanisms, where multiple interconnected factors collectively govern the overall process. A review of the literature reveals that the resulting morphology is strongly dependent on the type and nature of the dopant atom.

Bernardo et al. have produced Ga-doped ZnO nanostructures by the hydrothermal method. It was observed that Ga doping caused changes in the ZnO structure. The observed morphology is attributed to the selective adsorption of gallium species in the basal planes of ZnO, which inhibits growth along the $\pm [0001]$ direction. An excess of nitrates generally promotes the formation of large sizes of well-crystallized ZnO rods. It was observed that platelet formation was more advantageous as the ratio between acetate and nitrates from Zn^{2+} and Ga^{3+} precursors increased. They reported that nitrate excess could affect the axial growth of nanoplatelets, while growth inhibition along the c-axis would be associated with Ga^{3+} ions [45].

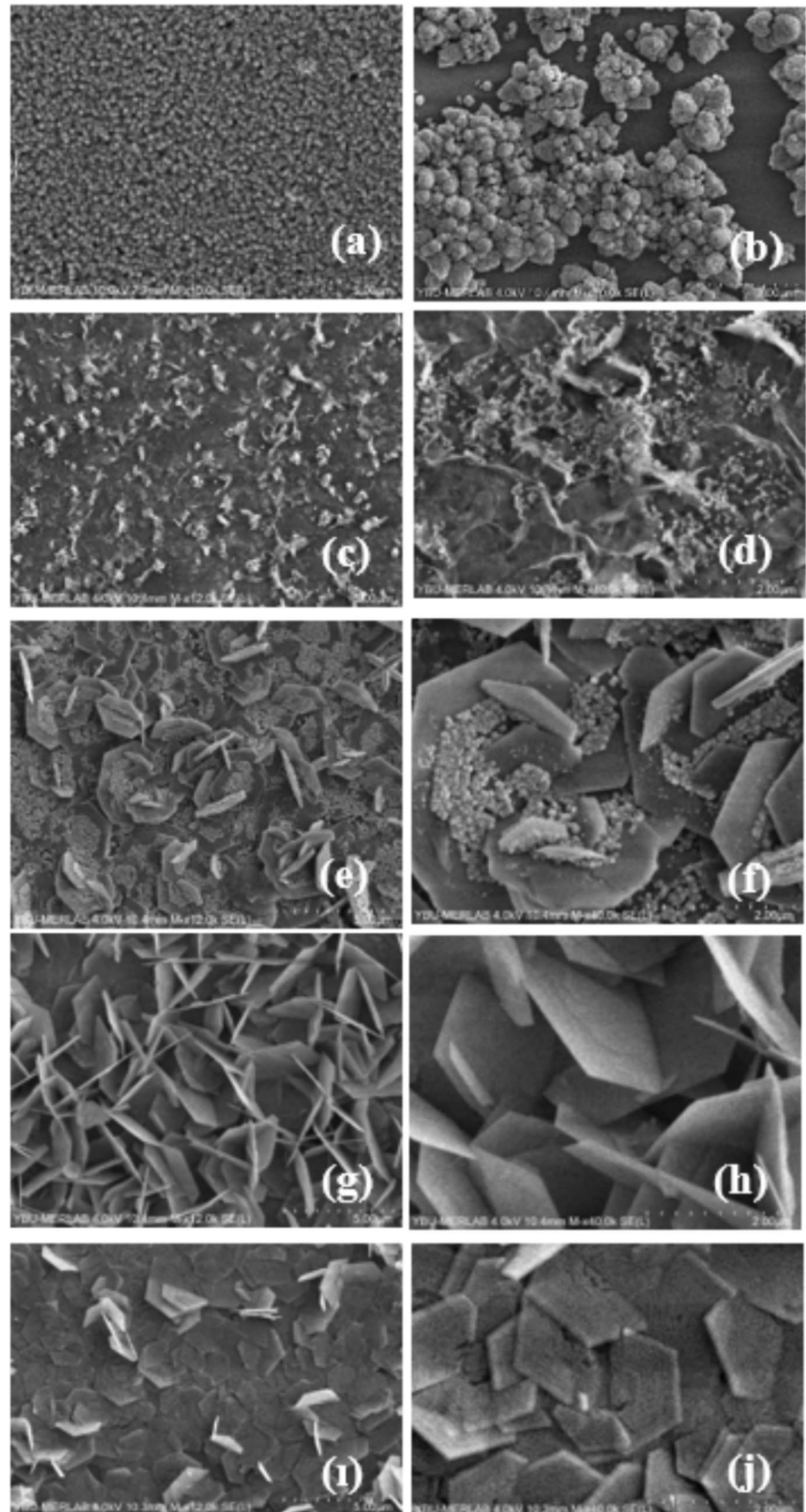
Song et al. have optimized the synthesis state of 1%, 3% and 5% Ga-doped ZnO nanowires (NWs) using hot-walled pulsed laser deposition (HW-PLD) incorporating facilitated kinetic energy control of

laser-cut particles. Using HW-PLD in morphology diversification, they obtained both zigzag-shaped NWs and nanohorns. The doping-enhanced pathway has been successfully developed, allowing them to report that the electrical properties of nanostructures can be designed without significant issues. As a practical application of highly sensitive nanosensors, they explained that the managed resistance of doped NWs will play a crucial role in simultaneous materials sensing by enhancing the sensing range (i.e., adjusting the sensitivity) and by combining NWs with different resistances [46].

In addition, a morphology change was observed in different doping atoms in the same way. Awad et al. have produced ZnO compounds that were used as precursors to prepare different nanostructures of indium (In)-doped ZnO by the melting method and using chemical vapor deposition (CVD) at different In doping ratios. At low indium concentrations, the replacement of Zn^{+2} ions with In^{+3} ions occurs, while at higher In ratios, In_2O_3 appears as a separate phase. The nanowires turn into nanoflakes and then into nanoflowers as the In concentration increases. The rate of crystal growth varies in different directions and is governed by $V[0001]$, $V[01]$, and $V[000]$. The addition of indium leads to a redistribution of surface energy and growth direction, where growth along the $[0001]$ direction decreases, resulting in the formation of nanoflakes and subsequently, nanoflowers. This means that In acts as a passivation agent through charge compensation, slowing ZnO growth along the $[0001]$ direction [47].

Pham et al. have grown ZnO thin films using the scattering method with co-doping of In and Ga. They reported that the thermoelectric properties of ZnO thin films can be reduced simultaneously with the co-doping of In and Ga. They reported that varying the In and Ga contents would not only optimize the carrier concentration associated with Fermi level modification but also regulate the lattice defects that contribute to the scattering transport mechanisms. Moreover, In^{3+} compensation in the substitution sites significantly increases the state density of the active mass due to flattening of the conduction band, especially at high temperatures. As a result, coupling modification of the Fermi level, band flattening, and lattice defects leads to moderate retention of electrical conductivity, an increase of the Seebeck coefficient, and a decrease of thermal conductivity, respectively [48].

Fig. 2 The SEM analyses of produced samples: pure ZnO (a, b), 2GZO (c, d), 4GZO (e, f), 6GZO (g, h), 8GZO (i, j)



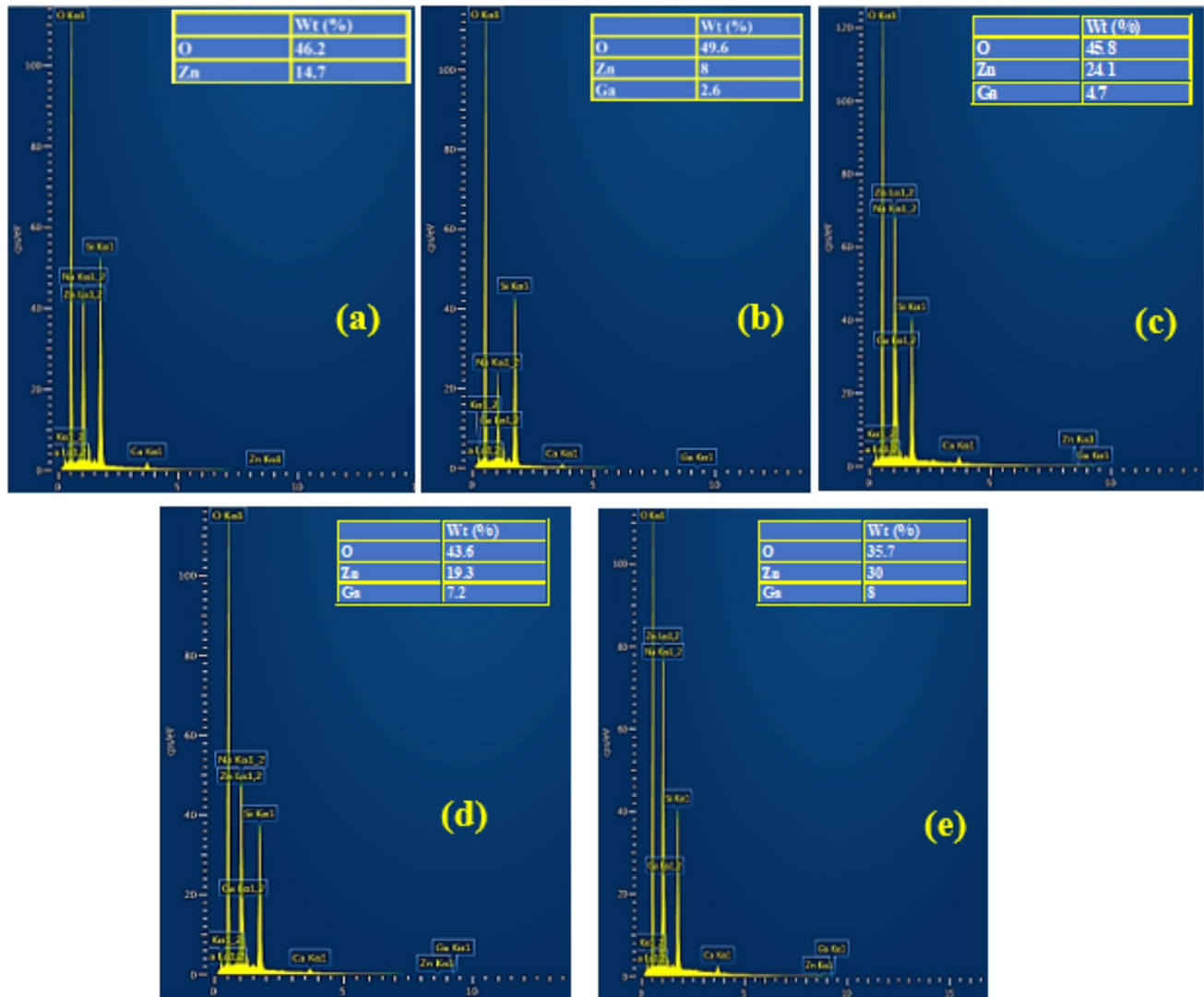


Fig. 3 The EDAX analysis of pure and Ga-doped ZnO thin films

Figure 3 depicts the EDAX analysis of pure and Ga-doped ZnO thin films. From the EDAX analyses, changes are observed in the ratios of Zn, Ga, and O elements in the samples depending on the contribution ratio. Additionally, EDAX analyses indicate that the samples were produced using the SILAR technique at stoichiometrically appropriate doping ratios. The Si, Na, C, and Ca in the analysis come from the glass substrate used during production.

Figure 4 shows the Raman spectra of the samples associated with the doping ratio. All of the spectra contain the usual wurtzite hexagonal structure Raman active modes, which are E_{2low} , $2E_{2low}$, E_{2high} , E_{2low} , E_{2high} , $A_1(LO)$, and E_g modes [49]. In addition, the phonon mode at 439 cm^{-1}

was red-shifted, which seems to be very sensitive to the Ga concentration. The phonon modes were found at 439 , 439 , 434 , and 431 cm^{-1} for ZnO, 2GZO, 4GZO, and 6GZO, respectively. There is no phonon mode for 8GZO. It can be confirmed with SEM and XRD results. The mode shifts reveal the successful incorporation of Ga ions into the ZnO lattice [50]. The inability to identify signals from other gallium oxides in Raman spectra indicates that no further gallium species impurities have developed and that the as-prepared nanocrystals have been successfully doped with Ga^{3+} ions [51]. E_{2low} (about 100 cm^{-1}) pertains to the lattice vibrations of zinc atoms. $2E_{2low}$ denotes the second-order phonon mode, while E_{2high} pertains to the lattice vibrations of

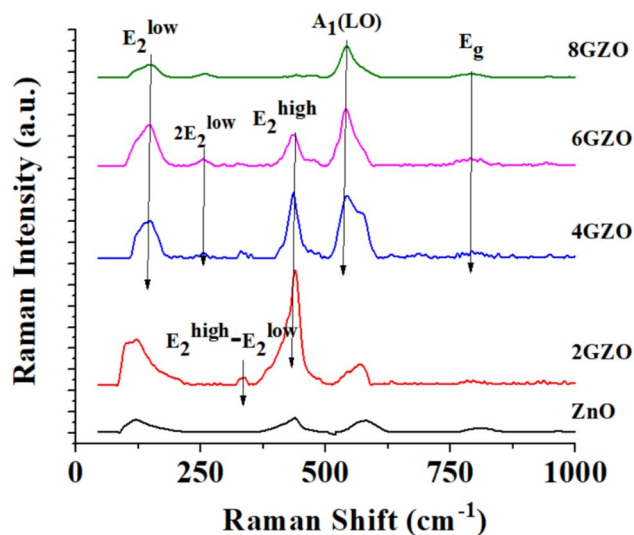


Fig. 4 The Raman spectroscopy of thin films

oxygen atoms (about $\sim 437 \text{ cm}^{-1}$). This peak is essential for the crystallinity of ZnO; its sharpness and height signify crystal purity. $A_1(\text{LO})$ (about 580 cm^{-1}) is typically linked to defects, including oxygen vacancies and zinc interstitials. Gallium doping can influence the magnitude of this peak. E_g (about $750\text{--}800 \text{ cm}^{-1}$) corresponds to the mode linked to the electron–phonon interaction. The $E_2(\text{high})$ peak is observed in pure ZnO, albeit with reduced intensity. The peak gets increasingly obvious and strong with Ga doping, signifying an enhancement of the crystal structure. The $A_1(\text{LO})$ peak varies with increasing Ga doping, signifying alterations in defect density associated with doping levels. The spectrum in 8GZO is

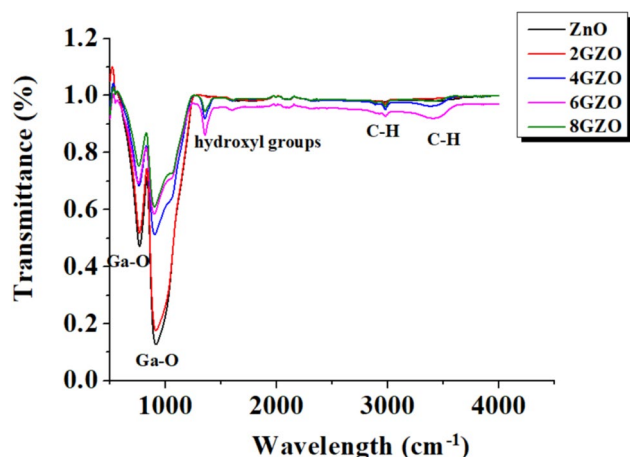


Fig. 5 FT-IR analysis of pure and doped ZnO films

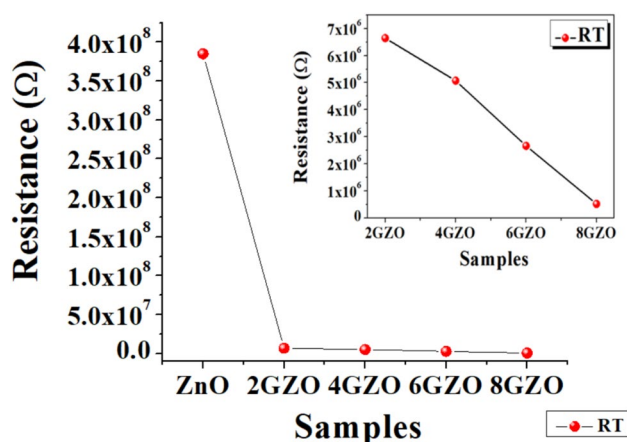


Fig. 6 Resistance versus pure and doped ZnO films at room temperature

more defined, suggesting that doping can enhance crystal quality to some degree [52].

FTIR analyses are shown in Fig. 5. The formation of wurtzite structures in all samples is supported by both FTIR and XRD results. An increase in the density of O–H absorption bands is observed as the Ga doping ratio in the samples increases [53]. This can be attributed to the reduction in particle size. As the ratio between O–H and Zn–O contents increases, the particle size changes, which can be attributed to the increase in the Ga doping ratio. The ratio of O–H/Zn–O intensities was calculated as 1.03, 1.03, 1.04, 1.16, and 1.25 for ZnO, 2GZO, 4GZO, 6GZO, and 8GZO, respectively [54]. The greater the particle size change, the less likely the OH group is to adhere to and desorb from the surface of the samples. It clearly reveals the shift in the Zn–O band in samples 445, 445, 451, 461, 451, and 471 cm^{-1} . It can be attributed to Zn–O stretching modes, and shifts are observed in these modes with doping. Moreover, the IR bands corresponding to O–H bending at $\sim 1350 \text{ cm}^{-1}$ reveal higher transmittance intensity in Ga-doped ZnO powders, which may be attributed to the variation in Zn^{+2} and Ga^{+3} radii along with the structural modifications induced by doping [54, 55]. Peaks detected at low wavenumbers, between 400 and 800 cm^{-1} (corresponding to Ga–O and Zn–O vibrations), are indicative of metal–oxygen bonding. With an increase in the Ga doping ratio, the peak position and intensity in this region may exhibit minor alterations, signifying the incorporation of Ga atoms into the Zn lattice. Peaks in this region between 1400 and 1700 cm^{-1} (hydroxyl groups—OH) signify

the presence of water molecules or hydroxyl groups adsorbed on the surface. C–H peaks in the range of 2800–3000 cm^{-1} , indicative of C–H stretching vibrations, typically arise from organic or solvent residues. With an increase in Ga concentration, the peak in the Ga–O region becomes markedly apparent. Variations in transmittance at hydroxyl groups suggest alterations in surface structure and adsorption capability due to doping [56, 57].

The resistance values of the samples at room temperature are given in Fig. 6. The resistances of the samples were calculated as 385 M Ω , 6640 k Ω , 5070 k Ω , 2670 k Ω , and 522 k Ω for ZnO, GZO2, GZO4, GZO6, and GZO8, respectively. When the graph is examined in detail, it can be seen that the resistance values of the samples decrease with increasing the ‘Ga’ ratio [58]. The positive valence charge created by replacement must be compensated for by the release of extra electrons to maintain charge neutrality, which enhances the abundance of unbound electrons and leads to a reduction in the electrical resistance of the metal-oxide [59, 60].

The operating temperature is a crucial parameter for studying gas sensors. The dynamic responses of the Ga-doped ZnO sensors were assessed at various NH_3 concentrations, as illustrated in Fig. 7 at room temperature. All graphs have exhibited variability in reaction regarding changes in resistance according to fluctuations in the concentration of gaseous molecules. The alteration in gas concentration significantly affected the conductance value (i.e., resistance value) of the sensing device, indicating a potential change in the interaction frequency of gaseous molecules with the surface and subsequent surface reactions. The performance of individual sensing devices was assessed by altering the doping concentration of Ga^{3+} ions in ZnO systems. In this regard, it is evident that clean ZnO nanospecimens demonstrate inferior performance compared to Ga^{3+} in terms of responsiveness. Sensors composed of 6% Ga-doped ZnO nanostructures had the most significant response in detecting NH_3 gas [61]. This can be attributed to the sudden alteration in charge carrier concentration inside the electronic structure of ZnO resulting from Ga^{3+} ion doping, as examined in the optical characteristics. Furthermore, the improved dynamic characteristics of the ZnO gas sensors were also achieved for Ga-doped ZnO [62]. The baseline resistance abruptly decreases upon the introduction of the target gas and thereafter rapidly

returns to its prior values once the gas chamber is evacuated and replenished with dry air. The reaction time is defined as the duration required for the response to fall below 90% of the equilibrium value after the administration of NH_3 . The recovery time refers to the duration required for the sensor to elevate its response to 10% over its starting value in dry air.

Figure 8 shows the sensing response of sensors exposed to different ammonia gas concentrations at room temperature. The response values of 25 ppm were calculated 18%, 20%, 68%, 94% and 13% for ZnO, 2GZO, 4GZO, 6GZO, and 8GZO, respectively. In ZnO, gas-sensing occurs primarily through oxygen vacancies (V_o). Doping increases electron density, facilitating oxygen adsorption. After a certain level of Ga doping, oxygen vacancies decrease due to charge balancing, eliminating active adsorption sites. Excessive carrier density (degeneration) excessively increases the free electron density, disrupting ZnO’s semiconductor behavior and rendering it a metal-like (degenerate) semiconductor [63].

The morphology of metal-oxide materials strongly influences the gas-sensing properties and varies depending on the synthesis method [64]. The choice of synthesis method is a crucial factor in obtaining the desired nanostructures, including morphology, grain/particle size, crystal structure, and optical and electrical properties [65]. In addition to morphology, chemical composition, and crystal structure, which are highly influential on gas-sensing properties, these factors have contributed to obtaining excellent gas-sensing properties in processes such as surface modification, doping, composite formation, and integration with functional materials [66].

On the other hand, another factor affecting the sensor performance is the porosity of the sensor film layer. In a compact layer, the gas cannot fully penetrate the sensing layer. Often, the reactions occur only on the film surface [67]. But in porous structures, gas can diffuse easily, and gas molecules can easily reach grains, so the interaction between gas molecules and grains increases. This allows the target gas to react over a larger surface area. Moreover, the time for the gas to be trapped in the sensing surface material is increased, thereby significantly improving the sensitivity [68]. The target gas adsorbs on a metal cluster, decomposes, and produces active atomic species. Such metals accelerate the chemical adsorption on the film surface and increase the diffusion of the

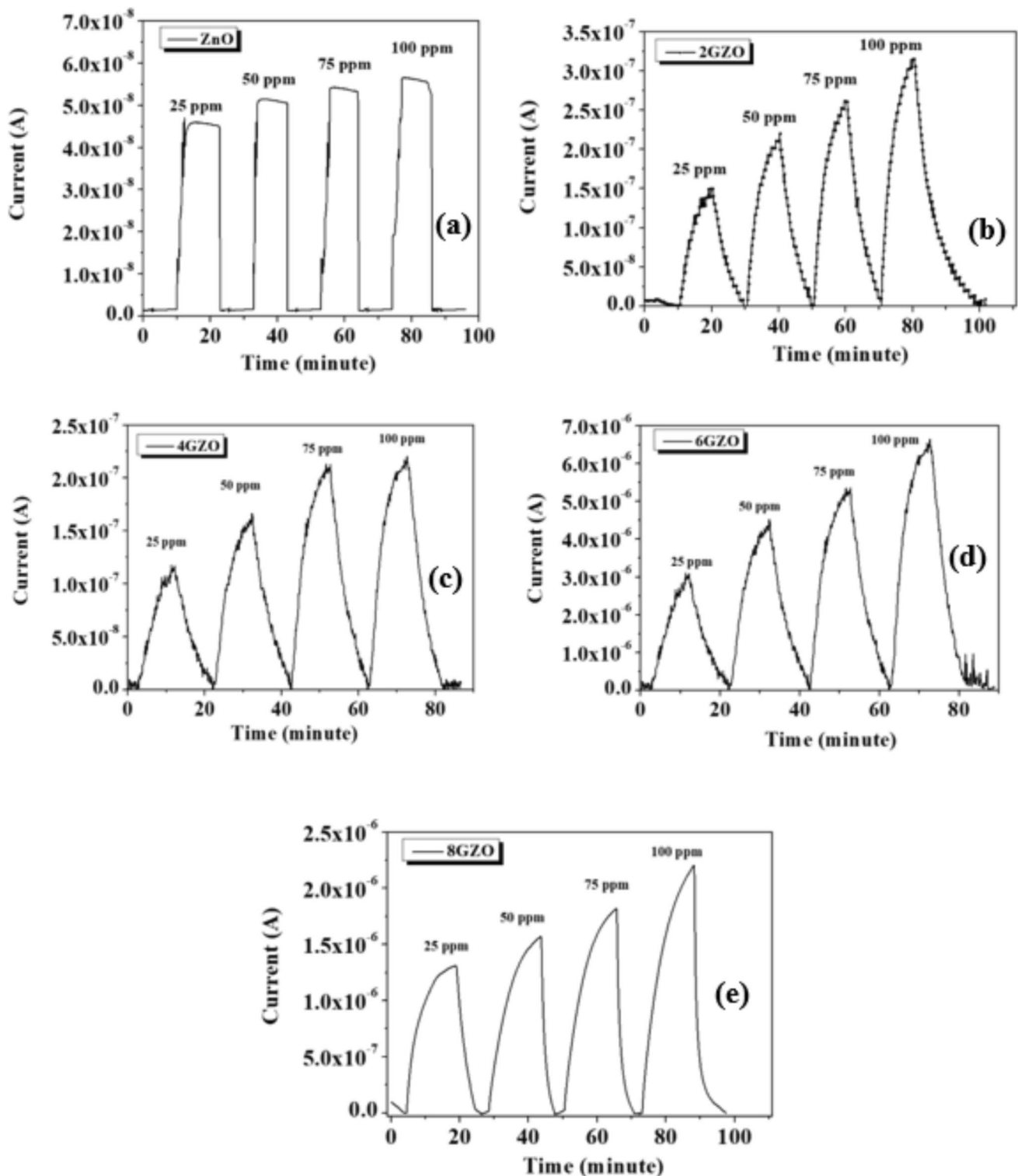


Fig. 7 Dynamic gas-sensing measurements for ZnO (a), 2GZO (b), 4GZO (c), 6GZO (d), and 8GZO (e) at room temperature

decomposed gas on the film surface. Thanks to the activated sensing surfaces, the sensitivity to the target gas increases. Moreover, the noble metal additive can

act as a catalyst in redox reactions, thereby improving the sensor's response and recovery times. The doping process can be achieved by the simultaneous

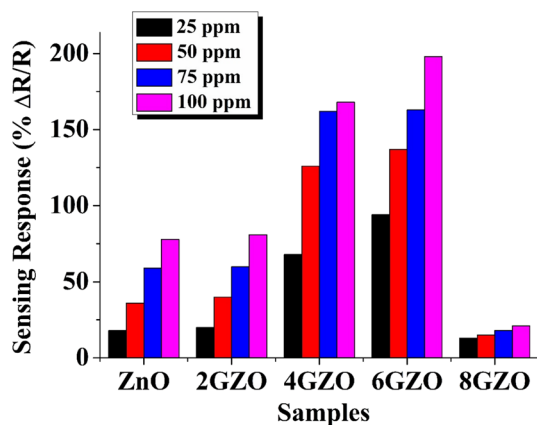
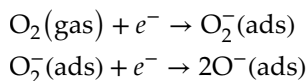


Fig. 8 Sensing response versus gas concentrations of the whole series of produced samples

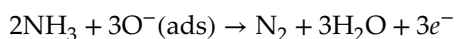
deposition of different metal or metal-oxide groups, or by creating layered structures [69].

As clearly seen in this study, both the electronic conductivity and the surface morphology of the films changed due to Ga doping. The gas-sensing mechanism is explained below in these two contexts: The gas-sensing behavior of GZO films toward NH_3 is primarily governed by surface adsorption–desorption reactions between the gas molecules and chemically active oxygen species on the ZnO surface. As an n-type semiconductor, ZnO's conductivity is strongly affected by the presence of adsorbed oxygen ions, which interact with target gases through redox processes [70, 71].

When the GZO sensor is exposed to air, oxygen molecules are adsorbed onto the surface and capture free electrons from the ZnO conduction band, forming negatively charged oxygen species such as O_2^- , O^- , or O^{2-} , depending on temperature [72]:



This electron withdrawal leads to the formation of an electron depletion layer (EDL) near the surface, which increases the sensor's resistance. When NH_3 gas is introduced, it acts as a reducing agent and reacts with these adsorbed oxygen species [73]:



During this reaction, electrons are released back into the ZnO conduction band, leading to a decrease in the depletion layer width and a reduction in resistance

(for n-type ZnO). This change in resistance is detected as the sensor's response to NH_3 .

Gallium doping plays several crucial roles in enhancing the ammonia sensing performance. Ga^{3+} ions substitute for Zn^{2+} in the lattice, introducing additional free electrons that increase the baseline conductivity and facilitate faster charge transfer during gas interaction [74]. SEM analysis often shows that Ga doping transforms ZnO morphology (e.g., from nanoflowers to nanodiscs), which increases the specific surface area and active adsorption sites, enhancing gas–solid interactions. The Ga dopants create oxygen vacancies and defect sites, which serve as active centers for O_2 adsorption, thereby increasing the number of reactive oxygen ions on the surface [75]. The additional charge carriers and surface defects accelerate the adsorption–desorption kinetics, resulting in faster response and recovery times. The overall sensing mechanism can be summarized as a modulation of surface resistance due to redox reactions between NH_3 molecules and adsorbed oxygen species. The combination of improved charge transfer, optimized morphology, and defect engineering through Ga doping enables a higher response magnitude and faster reaction kinetics.

In ZnO, gas-sensing occurs primarily through oxygen vacancies (V_o) [76]. Doping increases electron density, facilitating oxygen adsorption. After a certain level of Ga doping, oxygen vacancies decrease due to charge balancing, eliminating active adsorption sites. Excessive carrier density (degeneration) excessively increases the free electron density, disrupting ZnO's semiconductor behavior and rendering it a metal-like (degenerate) semiconductor. As observed in our data, the 6GZO exhibited the highest response (198% at 100 ppm NH_3 , room temperature), likely representing an optimal balance between charge carrier density and active surface area. Beyond this concentration (e.g., 8%), excessive doping can lead to defect clustering or reduced crystallinity, which hinders electron mobility and diminishes gas-sensing performance [68].

Figure 9 gives the response and recovery times of pure and doped ZnO samples. When response and return times were examined, faster results were obtained in the pure sample compared to the adulterated samples. While response and return times of 2 to 3 s were observed in the pure sample, they increased to 7 and 8 s in the doped samples. This phenomenon is due to the key juncture at which the catalytic efficacy of Ga attains its peak potential; inadequate Ga doping

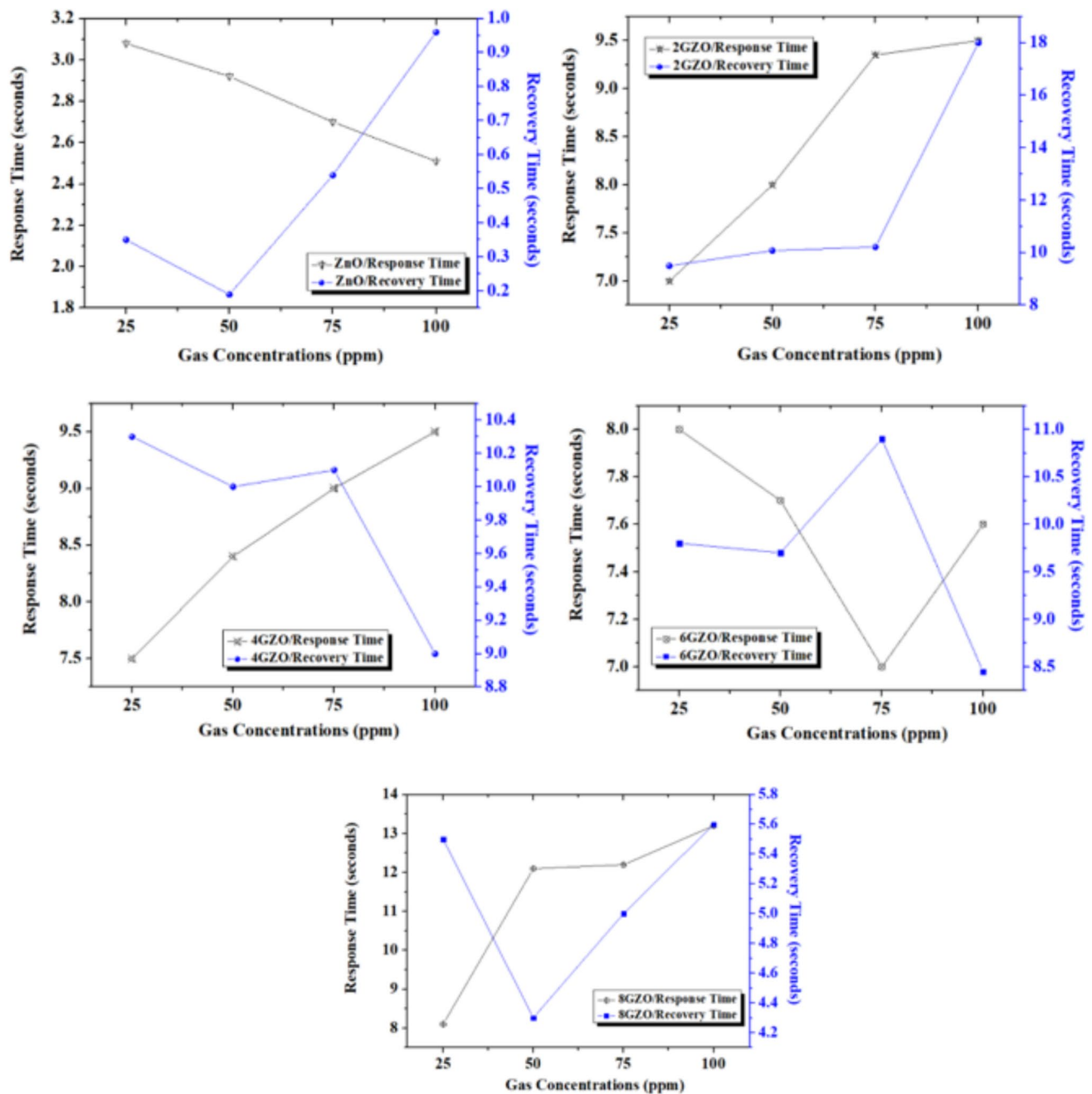


Fig. 9 Response and recovery time of pure and doped ZnO sensors

does not fully harness this effect, whilst excessive doping detrimentally impacts the gas sensitivity performance of the sensor [77–79]. The intricate relationship between Ga doping and sensor detection highlights a delicate balance that must be maintained for optimal performance. As the surface volume ratio increases, the sensor's ability to detect gases is significantly enhanced, allowing for more precise measurements.

However, this improvement reaches a peak when Ga doping levels are carefully calibrated; too little doping fails to harness the full potential of the material, while excessive amounts can detrimentally affect gas sensitivity. The response and recovery time also fluctuate with varying levels of Ga, suggesting that achieving peak catalytic efficacy requires a thoughtful approach to doping levels. Ultimately, understanding

these dynamics is essential for developing sensors that effectively combine sensitivity and efficiency in gas detection applications. This may occur from the instability in conductivity induced by the augmentation of dopants and the consequent alteration in response and recovery times.

The highest responses were obtained for 6GZO. As a result, the detailed gas-sensing properties of the 6GZO sensor were investigated. The addition of metal can lead to an increase in carrier concentration at the surface, and accordingly, an increase in surface defects. With the increase in surface defects, more adsorption sites for gas reactions are formed, resulting in a significant improvement in gas response [80]. Figure 10 gives the linearity of the 6GZO sensor. It exhibited linear sensitivity for each sensor. Since the effect of the chemical sensor against the gas is generally dependent on the interaction of the sensing film layer on the surface and the gas, the sensitivity value and response speed of the sensor will improve with the increasing surface area of the sensing film layer [81]. However, the size distribution and grain boundaries of nanoparticles also affect the sensor properties. In particular, the SEM analyses reveal that the square-shaped structures have thin, cornered edges. For this reason, it is thought that the gas interacts not only with the surface but also with each point of the film produced in 3D, especially in the 6GZO sample.

Figure 11 shows the repeatability of the 6GZO sensor. No shift in current values was observed over 10 cycles, except for very slight shifts. This demonstrates that the sample remains stable and does not deteriorate with use. In our case, it is evident that the physical adsorption mechanism prevails. Physical adsorption

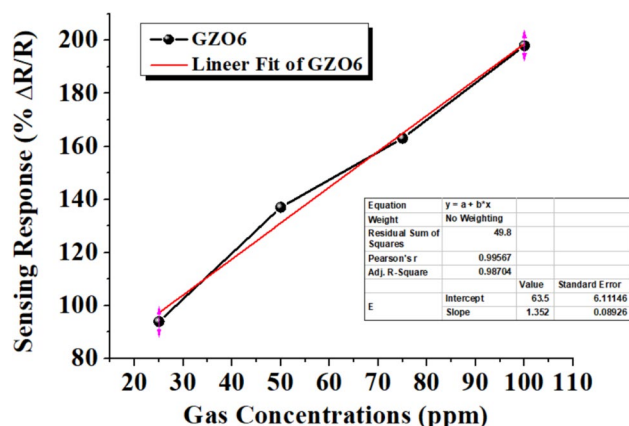


Fig. 10 The linearity of the 6GZO sensor

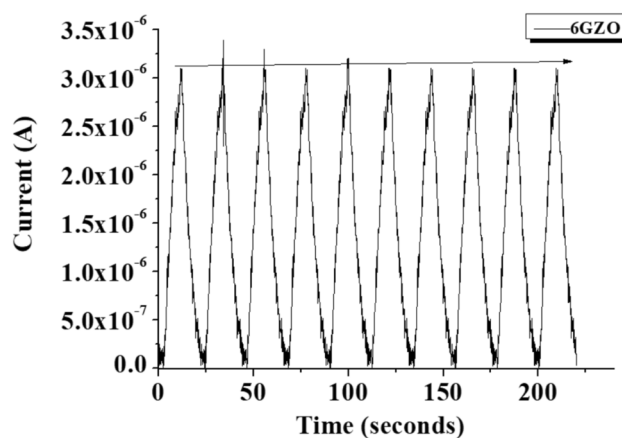


Fig. 11 The repeatability of the 6GZO sensor

has a very small activation energy and involves relatively weak Van der Waals interactions [82]. Therefore, it is a low-energy process. In the case of physical adsorption, the heat of adsorption is small; in contrast, the adsorbed molecules can be easily removed from the surface. In the case of chemical adsorption, however, this is very difficult. In the case of physical adsorption, an adsorbed layer is formed whose thickness is several times the diameter of the adsorbed molecules under suitable temperature and pressure conditions [83].

Figure 12 illustrates the reproducibility of the 6GZO sensor over time. Daily measurements were conducted using the 100 ppm NH_3 gas sensor, and the current values of these measurements were documented, as indicated by the repeatability data in Fig. 12. No alterations in current values were noted until day 10; however, a decline in current values commenced from day

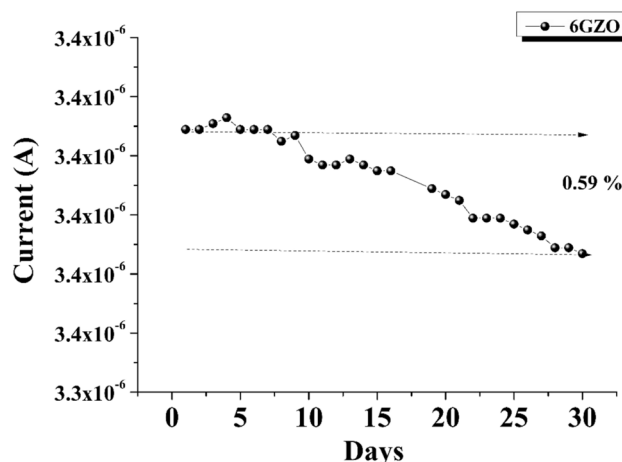


Fig. 12 The reproducibility of the 6GZO sensor

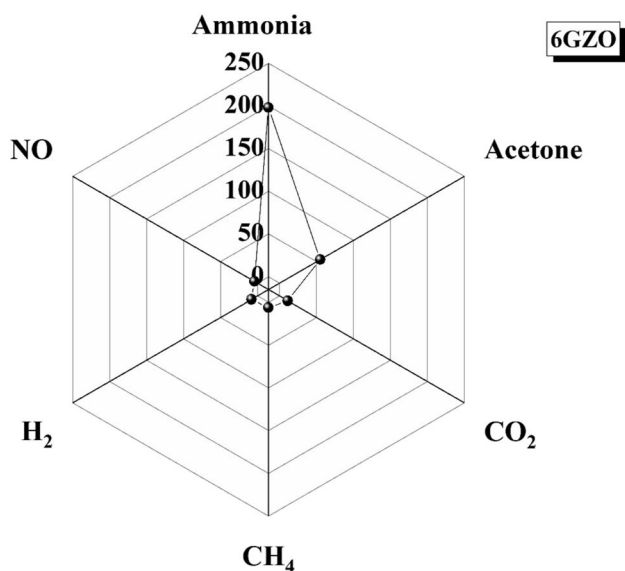


Fig. 13 The selectivity of the 6GZO sensor

10 onward. On day 30, the sample's value diminished from 3.38×10^{-6} to 3.36×10^{-6} . In the 6GZO sample, a 0.59% deviation was seen in the measured current value due to the presence of 100 ppm NH_3 gas.

Figure 13 illustrates the room-temperature sensor response of the 6GZO thin film to various gas types, presented as a radar diagram. The results reveal that the 6GZO film exhibits a significantly high sensitivity to ammonia (NH_3). The sensitivity measured on the NH_3 axis reaches approximately 198, while this value remains quite low for other gases. This clearly demonstrates that the 6GZO film is a highly selective sensor material for NH_3 .

When examining other gas types, the sensor response to acetone was found to be moderate (approximately 40–50%), while the response to gases such as NO , H_2 , CO_2 , and CH_4 was quite low (≈ 10 –20%). The minimal sensitivity, particularly to non-polar gases such as CH_4 and CO_2 , suggests that the Ga-doped ZnO surface exhibits limited interaction with these gases [84]. This selectivity can be explained by the fact that Ga doping alters the surface properties and electron density of ZnO. The substitution of Ga^{3+} ions for Zn^{2+} ions causes local charge irregularities in the crystal lattice and the formation of different adsorption centers on the surface. NH_3 molecules, due to their electron-donating nature, exhibit strong chemical interactions with these active surface sites. The electrons transferred to the sensor during adsorption significantly reduce the film resistance, resulting in a high sensor response. In contrast, non-polar or electron-accepting gases such as CO_2 and CH_4 have limited interaction with these surface centers, resulting in low sensitivity [85].

Generally speaking, a 6% Ga doping rate can be said to provide the optimal selectivity and sensitivity profile for ZnO-based sensors. This doping level allows for the formation of more adsorption centers on the surface and strong interactions with NH_3 molecules, while avoiding the negative effects that excessive doping can cause, such as increased conductivity and decreased surface active area. Therefore, it can be concluded that 6GZO film is an extremely suitable material for NH_3 sensor applications due

Table 2 The literature comparison studies of NH_3 gas sensors at room temperature for different doping materials

Sample	Production method	Concentration (ppm)	Gas response (%)	Response time (s)	Recovery time (s)	References
2% Mn-doped ZnO	a low-cost and fast solution combustion synthesis,	100	95.37	73	147	[86]
3% La-doped ZnO	spray pyrolysis method	50	74.28	17	30	[87]
2% Cu-doped ZnO	the facile drop-casting method,	250	32	70	15	[88]
2% doped La-doped ZnO	the facile drop-casting method,	250	70	68	11	[88]
3% Yttrium-doped ZnO	hydrothermal method	100	40	185	206	[72]
1% Ca-doped ZnO	Sol-gel	4000	33	5	221	[89]
3% Ti-doped ZnO	wet chemical synthesis using drop-casting technique	250	74	10.4	6.4	[90]
6% Ga-doped ZnO (6GZO)	SILAR	100	198	7.6	7	Present work

to its high NH_3 sensitivity and low cross-sensitivity properties.

Table 2 presents a comparison of literature studies on NH_3 gas sensors at room temperature for various doping materials. The innovative aspect of this study is reinforced by a comparative analysis table that juxtaposes our room-temperature (RT) performance with representative findings from the literature. Table 2 presents a comprehensive comparison of previously reported RT-operated doped ZnO-based NH_3 sensors in terms of key parameters such as sensitivity, response time, and recovery time. The 6GZO sensor developed in this work demonstrates advanced NH_3 detection capability, particularly with its high sensing response at room temperature, surpassing the performance values commonly reported in the literature. Moreover, the response and recovery times of the Ga-doped ZnO sensor are markedly more advantageous compared to similar ZnO-based sensors documented in earlier studies. The obtained results indicate that Ga-doped ZnO offers an effective approach for enhancing NH_3 gas-sensing behavior. Overall, this study represents a significant advancement among methodologies applied to improve the sensitivity and selectivity of metal-oxide nanomaterials, especially in terms of achieving lower detection limits and reduced response/recovery times.

4 Conclusion

In this work, Ga-doped ZnO thin films were grown by the SILAR Method, and their gas-sensing properties for NH_3 at room temperature were investigated. All samples exhibited a polycrystalline structure, with crystallization solely detected in the zincite configuration of ZnO. Diffraction peaks corresponding to the (100), (002), and (101) planes were observed in all films, aligning with JCPDS 36-1451 data. SEM investigations reveal a significant alteration in morphology contingent upon the Ga doping ratio. The nanoflower formations in undoped ZnO transform into hexagonal nanodisc structures upon the incorporation of Ga-doped atoms into the ZnO matrix. This change has a linear relationship with each contribution ratio. From Raman analysis, the mode shifts indicate the effective integration of Ga ions into the ZnO lattice. The $\text{E}_2(\text{high})$ peak is detected in pure ZnO; however, it has diminished strength. The peak becomes progressively more pronounced and robust with Ga doping,

indicating an improvement in the crystal structure. The $\text{A}_1(\text{LO})$ peak exhibits fluctuations as Ga doping levels increase, indicating changes in defect density that are linked to doping levels. The spectrum in 8GZO is more distinct, indicating that doping may improve crystal quality to a certain extent. The highest responses were obtained for 6GZO. The results indicate that sensitivities rise with sensor materials up to 6% doping, after which a decline is noted at 8% doping. Additional doping, specifically the enhancement of material capacity after 8GZO, does not result in a proportional increase in gas detection efficacy. The augmented Ga doping envelops the ZnO surface, hence influencing the effective contact area with gas molecules.

Moreover, excessive Ga doping might diminish the interaction between NH_3 molecules and the ZnO material, leading to a reduced response of the doped ZnO sensor.

Author contributions

Sezen Tekin: writing—original draft; investigation, formal analysis; visualization, Irmak Karaduman Er: formal analysis; visualization, writing—original draft; investigation, Selim Acar: software; data curation, conceptualization; writing—review and editing, resources.

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Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or per-

sonal relationships that could have appeared to influence the work reported in this paper.

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