

Optimization of ZnO Thin Films for Selective Ammonia Sensing at Room Temperature

Madanakumara H¹, Mamatha K.M.², Kusuma S³, Meti Bharathi ⁴, Mohanakumara L.B⁵

^{1,4}– Assistant Professor, Department of Physics, Dr. Ambedkar Institute of Technology, Bengaluru, Karnataka, India

⁵– Assistant Professor, Department of Physics, JSS Academy of Technical Education, Bengaluru, Karnataka, India

^{2,3}– Assistant Professor, Department of Chemistry, Dr. Ambedkar Institute of Technology, Bengaluru, Karnataka, India

Corresponding author: Madanakumara H, madhunnk@gmail.com

Abstract

The increasing demand for reliable detection of hazardous gases has driven the development of advanced sensing materials with enhanced sensitivity and selectivity. In this study, ZnO thin films, including undoped, cerium (Ce)-doped, indium (In)-doped, and Ce–In co-doped variants, were synthesized using the spray pyrolysis technique at an optimized temperature of 350°C. The influence of doping and morphology on the structural, optical, and gas sensing properties of the films was systematically investigated. X-ray diffraction analysis confirmed the crystalline nature and variation in crystallite size with dopant concentration, while FESEM studies revealed significant morphological transformations from spherical to hexagonal structures. Optical studies indicated tunable band gap and transmittance with doping. Gas sensing performance was evaluated for various volatile gases, with a strong response observed particularly toward ammonia (NH₃) at low concentrations. Among all samples, Ce–In co-doped ZnO thin films exhibited superior sensing characteristics, including higher sensitivity, faster response, and improved recovery time, attributed to increased surface area and optimized charge carrier dynamics. The findings highlight the critical role of morphology and dopant engineering in designing next-generation ZnO-based gas sensors for environmental monitoring and industrial safety applications.

Keywords: ZnO thin films, gas sensors, spray pyrolysis, doping, morphology, ammonia sensing, Ce doping, In doping, co-doped ZnO, nanostructured materials

How to cite this article: Madanakumara H, Mamatha KM, Kusuma S, Bharathi M, Mohanakumara LB. Optimization of ZnO Thin Films for Selective Ammonia Sensing at Room Temperature. *Int J Drug Deliv Technol.* 2026;16(62s): 997-1004. DOI: 10.25258/ijddt.16.62s.106

Source of support: Nil.

Conflict of interest: None.

1. Introduction:

The environment in which we live contains a wide variety of chemical species, both natural and man-made. While some of these are essential for sustaining life and supporting human activities, many others are harmful to varying degrees. In the modern era, rapid industrialization has led to the extensive use and production of highly hazardous substances, particularly toxic and flammable gases. Accidental gas leaks can occur during industrial processes, posing serious risks to industrial facilities, workers, and nearby populations. Incidents involving asphyxiation, explosions, and loss of life continue to highlight the severity of these hazards worldwide. Therefore, the development and implementation of gas sensors are crucial for preventing such disasters.

Gas sensors play a vital role in modern technological systems where monitoring and controlling gas concentrations are essential. They are widely used across numerous sectors, including chemical and petrochemical industries, environmental monitoring

agencies, research laboratories, healthcare institutions such as hospitals, food and beverage industries, and microelectronics, including semiconductor manufacturing and telecommunications. Additionally, gas sensors are important in agriculture, transportation industries (automotive, marine, and aerospace), and power generation systems.

One of the primary advantages of gas sensors is their ability to detect gas leaks and integrate with automated control systems. In the event of a gas leak, sensors can trigger alarms or warning signals, enabling workers to evacuate safely and allowing systems to shut down automatically. This significantly reduces the risk of accidents, thereby protecting both human lives and industrial equipment. Gas sensors are also effective in detecting volatile and flammable gases, making them essential tools in fire prevention and safety management. They are commonly installed in oil refineries, gas storage facilities, pipelines, and exhaust systems.

Environmental monitoring is another critical application of gas sensors. Air pollution caused by industrial emissions and vehicle exhaust can be effectively monitored and controlled using these devices. Harmful gases such as nitrogen oxides (NO and NO₂), carbon monoxide (CO), sulfur oxides (SO_x), and ozone (O₃) are major contributors to environmental degradation. Emissions from coal-fired power plants release NO_x and SO_x gases, which can lead to acid rain and global warming. Additionally, photochemical reactions involving these gases contribute to urban smog formation. Monitoring and reducing these pollutants are essential for maintaining environmental and public health.

Gas sensors are also widely used in combustion systems to optimize fuel efficiency and reduce emissions. Sensors capable of detecting gases such as CO, NO_x, oxygen (O₂), carbon dioxide (CO₂), hydrocarbons (HCs), and volatile organic compounds (VOCs) enable precise control of combustion processes. This leads to improved energy efficiency, reduced fuel consumption, and lower emission of harmful gases.

Currently, gas sensors are designed to detect a broad range of gases, including ammonia (NH₃), arsine (AsH₃), bromine (Br₂), carbon dioxide (CO₂), carbon monoxide (CO), chlorine (Cl₂), chlorine dioxide (ClO₂), diborane (B₂H₆), fluorine (F₂), germanium tetrahydride (GeH₄), halocarbons (refrigerants), hydrocarbons (such as methane, ethane, and propane), hydrogen (H₂), hydrogen chloride (HCl), hydrogen cyanide (HCN), hydrogen fluoride (HF), hydrogen sulfide (H₂S), mercury vapor (Hg), nitrogen dioxide (NO₂), nitric oxide (NO), ozone (O₃), phosphine (PH₃), silane (SiH₄), sulfur dioxide (SO₂), organic solvents such as acetone and ethanol, and water vapor (H₂O).

In summary, gas sensors are indispensable in ensuring safety, environmental protection, and efficient industrial operations. Their ability to detect and monitor hazardous gases plays a crucial role in preventing accidents, reducing pollution, and improving the overall quality of life.

Overview of present work:

The main aspiration of the work is to preparation of nanocrystalline ZnO thin films using a spray pyrolysis technique and to investigate their structural, morphological, optical and NH₃ sensing properties.

In this research work, ZnO-based nanocrystalline thin films were developed for room-temperature gas sensing applications. Initially, undoped ZnO thin films were prepared using the spray pyrolysis technique at an optimized temperature of 350°C. The synthesized films were systematically characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray analysis (EDX), UV-Visible spectroscopy, and gas sensing measurements

to evaluate their structural, morphological, compositional, optical, and sensing properties.

To enhance the performance of ZnO thin films, cerium (Ce) and indium (In) were introduced as dopants to modify their surface morphology and functional characteristics. Subsequently, Ce-doped ZnO and In-doped ZnO thin films were prepared and characterized using the same set of analytical techniques. Furthermore, indium-cerium co-doped ZnO thin films were synthesized to achieve improved morphological control and enhanced gas sensing performance compared to undoped and singly doped films. These co-doped films were also thoroughly analyzed using XRD, FESEM, EDX, UV-Visible spectroscopy, and gas sensing studies. This systematic approach enabled a comprehensive understanding of the influence of doping and co-doping on the structural, optical, and gas sensing properties of ZnO-based nanocrystalline thin films.

2. Literature Review:

Several studies have explored the gas sensing properties of ZnO-based thin films using different dopants and preparation techniques. Rajendra S. Gaik et al. (2013) investigated liquefied petroleum gas (LPG) sensing using ZnO thin films prepared by spray pyrolysis in the temperature range of 300–500°C, employing zinc acetate as a precursor and a methanol-water mixture as solvent (0.5 M). Characterization using XRD, UV-Vis spectroscopy, SEM, and EDX revealed that crystallite size increased from 32.14 nm to 39.61 nm with increasing temperature, while optical absorption and band gap decreased. SEM analysis showed dense, spherical particles, and EDX confirmed the presence of Zn and O. The film prepared at 450°C exhibited superior LPG sensing performance.

Shewale et al. (2013) studied H₂S sensing using Cu-doped ZnO thin films synthesized by spray pyrolysis. Characterization through XRD, TEM, FESEM, and EDS indicated a polycrystalline hexagonal wurtzite structure with preferred orientation along the (002) plane. Morphological analysis showed transformation to more regular particle shapes with increased dopant concentration. The maximum gas response was observed at 4 wt% doping, with a response value of 0.08 at 20 ppm and 573 K.

Ganesh Kumar et al. (2013) reported ammonia sensing properties of Cu-doped ZnO thin films prepared using zinc acetate dihydrate as precursor. XRD results showed a decrease in crystallite size with increasing dopant concentration, while FESEM images revealed spherical particles with enhanced porosity. The films exhibited a strong response toward NH₃, with a response value of 1667 and response/recovery times of 30 s and 12 s, respectively.

Satish et al. (2011) examined the effect of aluminum doping on ZnO thin films prepared via spray pyrolysis. XRD analysis indicated a decrease in

(002) peak intensity with increasing Al concentration. SEM and TEM studies showed spherical particles (~800 nm), and XPS confirmed the presence of Al³⁺. The films demonstrated excellent sensitivity toward H₂S, with a response of 2600 at 1000 ppm.

Mariappan et al. (2013) investigated the influence of molar concentration (0.05M–0.15M) on ZnO thin films prepared using nebulizer spray pyrolysis. XRD analysis showed polycrystalline nature with increased (002) orientation and a maximum crystallite size of 77 nm. SEM images revealed uniformly distributed, plate-like structures with good porosity. The band gap was measured as 3.3 eV, and the films exhibited an ammonia response of 24.8 at 200 ppm and 50°C.

Ganesh Kumar et al. (2014) studied ammonia sensing using pure and Ni-doped ZnO thin films prepared by spray pyrolysis and post-annealed. Characterization techniques such as XRD, SEM, UV–Vis, AFM, and EDS confirmed structural and compositional properties. Crystallite sizes were found to be 28 nm (undoped) and 33 nm (Ni-doped). SEM and AFM analyses showed increased porosity and irregular grain distribution in doped films. The band gap decreased slightly with doping. Gas sensing studies indicated enhanced NH₃ sensing performance in Ni-doped films, with improved response and recovery characteristics compared to undoped ZnO.

Various approaches have been explored for detecting different gases, with surface morphology playing a crucial role in determining gas sensing performance. Zinc oxide (ZnO) is widely recognized as an effective sensing material due to its eco-friendly nature, low cost, and excellent chemical and physical properties. ZnO thin films can be synthesized using several techniques, including spin coating, dip coating, and spray pyrolysis.

Among these methods, spray pyrolysis offers significant advantages over spin and dip coating techniques. In spin and dip coating, the film deposition process is largely manual, making it difficult to achieve uniform coatings and limiting precise control over processing conditions, particularly temperature. In contrast, spray pyrolysis is a programmable technique that enables uniform thin film deposition with controlled parameters such as substrate temperature, precursor flow rate, and concentration. The ability to control temperature during film formation is especially important, as it directly influences the crystallinity, grain size, and surface morphology of the material, which in turn affect gas sensing performance.

Furthermore, the surface morphology of ZnO thin films can be effectively tailored through doping. The incorporation of suitable dopants modifies the structural and surface properties, enhancing gas adsorption, sensitivity, and overall sensor efficiency.

2.1 Experimental Characterization Techniques

Nanostructured semiconducting materials can be synthesized using a variety of physical and chemical methods, and their structural, morphological, and electronic properties are highly dependent on the synthesis technique. Therefore, systematic characterization is essential to understand the properties and performance of the prepared materials. Accurate interpretation of experimental results is crucial for correlating material characteristics with their functional behavior.

In this study, a range of characterization techniques has been employed to analyze the synthesized ZnO-based thin films. These techniques provide insights into crystal structure, surface morphology, elemental composition, optical properties, and gas sensing performance. The fundamental principles and applications of each method are briefly discussed.

The primary characterization techniques used in this work include:

- X-ray diffraction (XRD) for structural analysis
- Field emission scanning electron microscopy (FESEM) for surface morphology
- Energy dispersive X-ray analysis (EDAX) for elemental composition
- UV–Visible spectroscopy for optical properties
- Gas sensing measurements for evaluating sensor performance

2.2 Gas Sensing Studies

A gas sensor is a transducer that detects gas molecules and converts their concentration into a measurable electrical signal. The magnitude of this signal is directly proportional to the concentration of the target gas.

Several key parameters are used to evaluate gas sensing performance:

- **Sensor Resistance:** This describes the variation in electrical resistance (or conductivity) with gas concentration, typically expressed in parts per million (ppm).
- **Sensitivity (Response):** Sensitivity is defined as the ratio of resistance in air (R_a) to resistance in the presence of gas (R_g). A sensor exhibits high sensitivity if a small gas concentration produces a significant change in resistance. For n-type semiconductors, resistance decreases in reducing gases, whereas for p-type semiconductors, it increases.
- **Response and Recovery Time:** Response time is the duration required for the sensor to reach maximum resistance change upon

gas exposure, while recovery time is the time taken to return to its initial state after removal of the gas.

- **Operating Temperature:** The sensing performance depends strongly on temperature, as each gas-sensor combination exhibits maximum sensitivity at a specific temperature.
- **Adsorption Mechanism:** Gas sensing is governed by adsorption of gas molecules on the sensor surface, followed by surface reactions. Adsorption can be physical (low binding energy, reversible at low temperatures) or chemical (higher binding energy, requiring elevated temperatures).
- **Selectivity:** The ability of a sensor to preferentially detect a specific gas.
- **Stability:** The consistency and repeatability of sensor response over extended operation.

Gas sensing measurements were carried out using a custom-built setup consisting of a gas chamber (1 L volume), picoammeter, high-voltage power supply, and vacuum pump. The ZnO thin film sensor was initially stabilized in ambient air to establish a baseline resistance. Subsequently, a known concentration of NH₃ gas was introduced into the chamber using a microsyringe, and the corresponding change in resistance was recorded.

Aluminium foil was used as an electrode material due to its non-reactive nature and minimal interaction with the thin film. Electrical contacts were established using crocodile clips connected to a picoammeter. The sensor was placed inside the chamber, exposed to the test gas, and the current readings were measured to calculate the resistance changes.

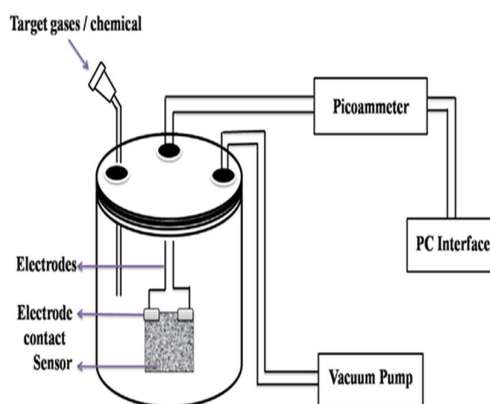


Figure 1: Block diagram of a sensing set up

3. Materials and Methodology:

In this chapter, ZnO thin films were prepared at different molar concentrations (0.05 M, 0.1 M, and 0.15 M), and their structural, morphological,

compositional, optical, and gas sensing properties were systematically investigated at room temperature under varying gas concentrations.

Nanoporous semiconducting metal oxides have attracted significant attention for gas sensing applications due to their high surface-to-volume ratio and uniform porosity, which enhance gas adsorption and reaction kinetics. Materials such as ZnO, WO₃, TiO₂, and SnO₂ are widely used as chemiresistive gas sensors for detecting hazardous gases in industrial environments, automobile emissions, and indoor air quality monitoring. Among these, ZnO is particularly promising due to its low cost, non-toxicity, and excellent electrical and chemical properties.

The gas sensing mechanism in metal oxides is based on the interaction between gas molecules and the sensor surface, leading to changes in electrical conductivity. A higher surface area and controlled porosity significantly improve sensitivity by increasing the number of active sites available for gas adsorption. Additionally, gas transport within nanoporous structures is governed by diffusion mechanisms, such as Knudsen diffusion, which depend on pore size and structure. Therefore, controlling the morphology and porosity of ZnO through suitable synthesis techniques is essential for enhancing gas sensing performance.

Various synthesis methods, including sol-gel, chemical vapor deposition, precipitation, and spray pyrolysis, are employed to fabricate ZnO thin films. Among these, spray pyrolysis is advantageous due to its simplicity, cost-effectiveness, and ability to produce uniform and porous films with controlled properties.

3.1 Experimental Details

ZnO nanostructured thin films were synthesized using the spray pyrolysis technique with zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] as the precursor. The films were prepared at molar concentrations of 0.05 M, 0.1 M, and 0.15 M on glass substrates maintained at a temperature of 350°C.

The precursor solution was prepared by dissolving zinc acetate dihydrate in 25 ml of double-distilled water, followed by continuous stirring for 30 minutes at room temperature using a magnetic stirrer. The resulting homogeneous solution was then loaded into the spray pyrolysis system.

Glass substrates of size 25 × 25 mm² were ultrasonically cleaned and placed on a heated substrate holder. The distance between the spray nozzle and the substrate was maintained at 16 cm, and a constant solution flow rate of 2 ml/min was used throughout the deposition process. Compressed air was employed as the carrier gas to atomize the precursor solution into fine droplets. These droplets were sprayed onto the heated substrate, where thermal decomposition occurred, leading to the formation of ZnO thin films.

4. Results and Discussion

4.1 X-ray Diffraction (XRD) Analysis

Figure 4.1 shows the XRD patterns of pure ZnO thin films prepared at different molar concentrations (0.05 M, 0.1 M, and 0.15 M). The observed diffraction peaks confirm the polycrystalline nature of the films with a hexagonal wurtzite crystal structure. Prominent peaks corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes were identified and are in good agreement with standard JCPDS data (card no. 89-1397).

Among the samples, the thin film prepared at 0.1 M concentration exhibits the highest peak intensity, particularly along the (002) plane, indicating a strong preferential orientation along the c-axis. This preferred orientation can be explained by the “survival of the fastest” growth mechanism. In contrast, the intensities of other planes such as (100), (101), (102), (110), (103), and (112) were found to be higher in the 0.15 M sample compared to the 0.05 M and 0.1 M films.

The diffraction peaks were observed at 2θ values of 31.96° , 34.53° , 36.29° , 56.74° , 62.95° , and 68.32° , corresponding to d-spacing values of 2.798 Å, 2.595 Å, 2.473 Å, 1.621 Å, 1.475 Å, and 1.372 Å, respectively. Additionally, the 0.1 M ZnO thin film exhibited relatively larger grain size compared to the other concentrations, which is consistent with the surface morphology results.

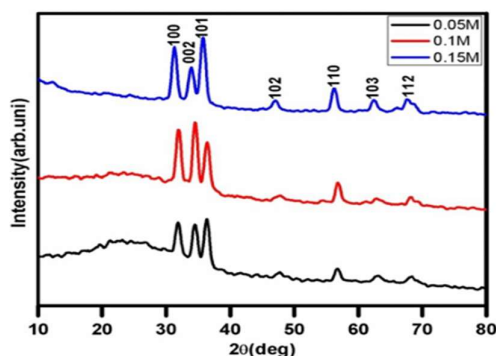


Figure 2: XRD patterns of spray deposited ZnO thin film

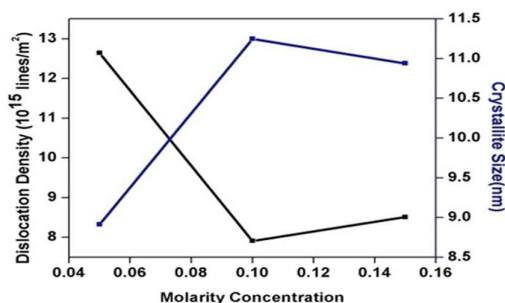


Figure 3: Variation of dislocation density and crystallite size with molar concentration

The structural parameters of ZnO thin films, including crystallite size (D), dislocation density (δ), and microstrain (ϵ), were calculated from the XRD data and are summarized in Table 4.1. The crystallite size was found to increase with molar concentration

up to 0.1 M and then decrease at 0.15 M, as illustrated in Fig. 2. All the films exhibit a hexagonal wurtzite crystal structure, as confirmed from the XRD patterns (Fig. 1).

The crystallite size was calculated using the Debye–Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the wavelength of X-rays, β is the full width at half maximum (FWHM), and θ is the Bragg angle. The dislocation density (δ), which represents the defect density in the crystal, was determined using the relation:

$$\delta = \frac{1}{D^2}$$

and the microstrain (ϵ) was estimated using:

$$\epsilon = \frac{\beta}{4 \tan \theta}$$

The variation of crystallite size and dislocation density with molar concentration is presented in Fig. 2, showing an inverse relationship between these parameters.

Table 4.1: Micro structural parameters of pure ZnO thin films at different molarity concentrations

| Concentration | Crystallite Size (D) (nm) | Dislocation Density ($\delta \times 10^{15} \text{ m}^{-2}$) | Microstrain ($\sigma \times 10^{-3}$) |
|---------------|---------------------------|--|---|
| 0.05 M | 8.91 | 12.64 | 3.19 |
| 0.1 M | 3.89 | 11.25 | 7.91 |
| 0.15 M | 3.09 | 10.94 | 8.51 |

4.2 Morphological Analysis

FESEM images of ZnO thin films prepared at 0.05 M, 0.1 M, and 0.15 M concentrations are shown in Fig. 4.3, Fig. 4.4, and Fig. 4.5, respectively. The images reveal that all the films consist of uniformly distributed spherical particles with no significant defects.

For the 0.05 M and 0.15 M samples, the particles are densely packed, resulting in relatively compact film structures. In contrast, the 0.1 M thin film exhibits a more uniform and well-defined surface morphology, with loosely packed grains and clear grain boundaries. This improved inter-grain uniformity enhances the porosity of the film.

The increased porosity in the 0.1 M sample provides a larger active surface area, which facilitates better gas adsorption and diffusion. As a result, this

morphology is favorable for improved gas sensing performance, particularly for NH₃ detection.

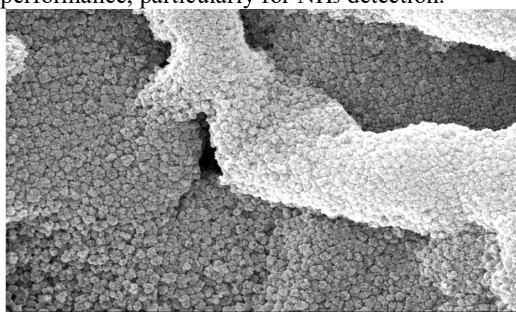


Figure 3: FE-SEM image of 0.05M ZnO film

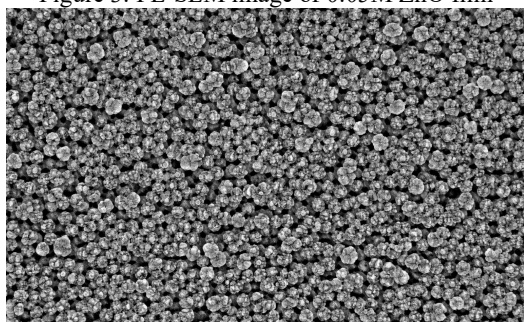


Figure 4: FE-SEM image of 0.1M ZnO film

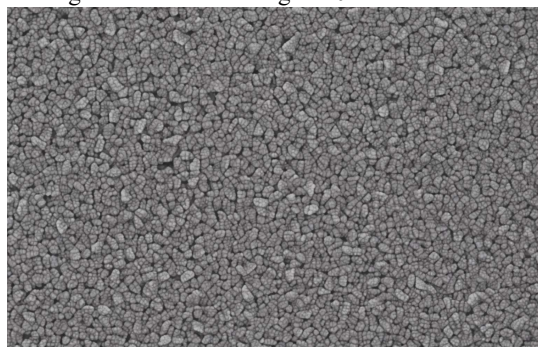


Figure 5: FE-SEM image of 0.15M ZnO film

4.3 Gas sensing performance of ZnO films

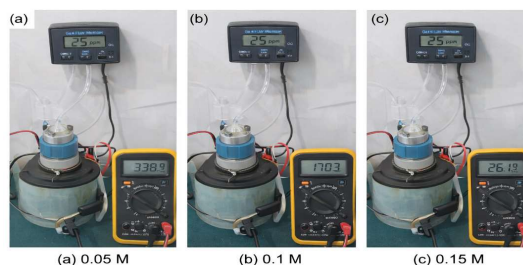
The gas sensing performance of nanocrystalline ZnO thin films prepared at different molar concentrations (0.05 M, 0.1 M, and 0.15 M) was evaluated toward NH₃ gas at room temperature. The PCD image clearly illustrates the comparative sensing response of the three samples under identical experimental conditions. Among all the concentrations, the 0.1 M ZnO thin film exhibited the highest response, indicating superior sensing efficiency.

This enhanced performance can be attributed to its optimized surface morphology, as confirmed by FESEM analysis. The 0.1 M sample possesses uniformly distributed spherical grains with well-defined grain boundaries and higher porosity, which significantly increases the active surface area available for gas adsorption. The larger number of

adsorption sites facilitates effective interaction between NH₃ molecules and the ZnO surface, leading to a pronounced change in electrical resistance.

In comparison, the 0.05 M and 0.15 M samples show relatively lower sensing responses due to reduced porosity and less favorable surface structure. The faster response and recovery characteristics observed for the 0.1 M sample further confirm its efficient charge transfer kinetics and rapid surface reaction mechanism.

Therefore, the PCD results strongly support that the 0.1 M ZnO thin film is the optimized composition for selective ammonia sensing at room temperature.



4.4 Optical Measurements

The optical transmittance spectra of ZnO thin films prepared at concentrations of 0.05 M, 0.1 M, and 0.15 M were recorded in the wavelength range of 350–800 nm, as shown in Fig. 4.7. All the films exhibit high transparency in the visible region, indicating their suitability for optoelectronic applications.

The transmittance values were observed to decrease from approximately 80% to 45% with increasing molar concentration. This reduction in transmittance can be attributed to enhanced photon scattering caused by increased film thickness, grain size variations, and structural inhomogeneities at higher concentrations.

Thus, thin films prepared at lower molar concentrations exhibit higher optical transmittance, whereas increased concentration leads to reduced transparency due to increased light scattering within the film.

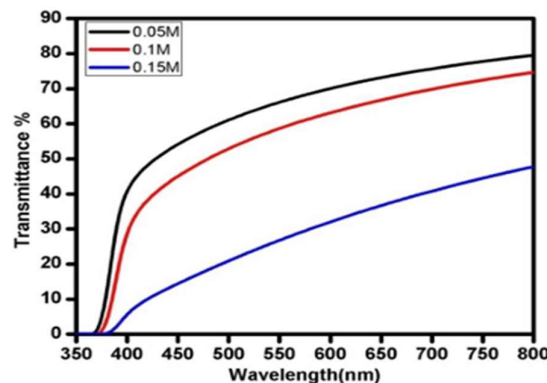


Figure 6: Optical transmittance spectra of ZnO films

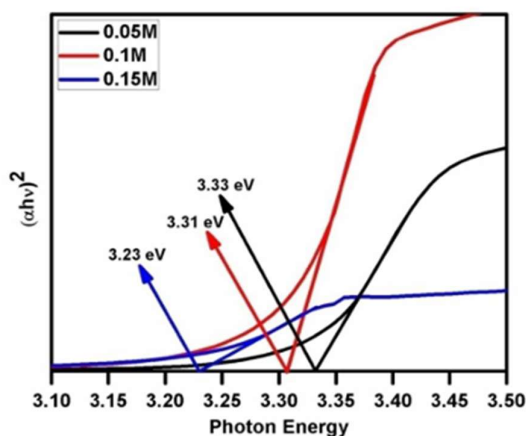
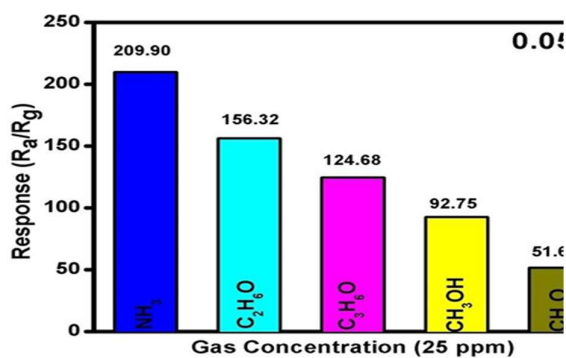
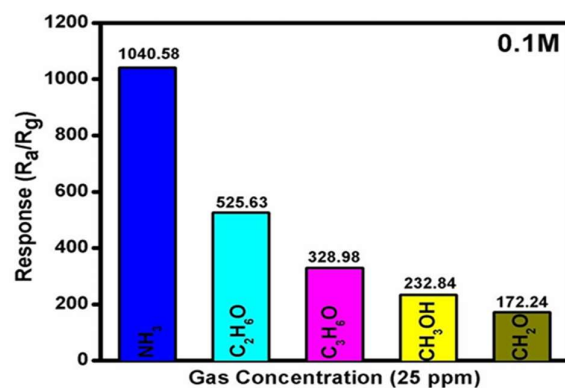
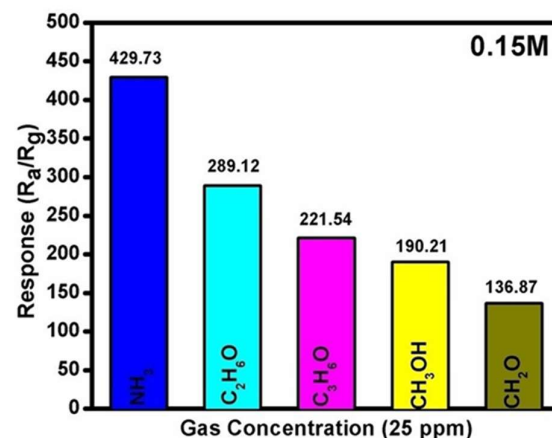


Figure 7: Optical band gap of ZnO films

4.5 Selectivity of NH₃

Gas sensing studies of ZnO thin films prepared at concentrations of 0.05 M, 0.1 M, and 0.15 M were performed for various gases at 25 ppm, including ammonia (NH₃), ethanol (C₂H₆O), acetone (C₃H₆O), methanol (CH₃OH), and formaldehyde (CH₂O), as shown in Fig. 4.16–4.18. The sensor responses for the 0.05 M thin film were 209.90, 156.32, 124.68, 92.75, and 51.69, respectively. For the 0.1 M thin film, significantly higher responses of 1040.58, 525.63, 328.98, 232.84, and 172.24 were observed. In the case of the 0.15 M thin film, the responses were 429.73, 289.12, 221.54, 190.21, and 136.87. Among all samples, the 0.1 M ZnO thin film exhibited the highest response toward NH₃. This enhanced selectivity is attributed to its improved surface morphology, characterized by uniform particle distribution and increased porosity compared to the 0.05 M and 0.15 M films. The higher porosity provides more active sites for gas adsorption, thereby enhancing the sensing performance toward ammonia.


 Figure 8: 25ppm of NH₃, C₂H₆O, C₃H₆O, CH₃OH and CH₂O at 0.05 M

 Figure 9: 25ppm of NH₃, C₂H₆O, C₃H₆O, CH₃OH and CH₂O at 0.1 M

 Figure 10: 25ppm of NH₃, C₂H₆O, C₃H₆O, CH₃OH and CH₂O at 0.15 M

4.6 TEM Analysis

The TEM images illustrate the morphological evolution of nanocrystalline ZnO thin films deposited at different precursor concentrations of 0.05 M, 0.1 M, and 0.15 M using the spray pyrolysis technique. These images provide valuable insights into particle size, distribution, and surface characteristics, which are crucial for understanding the material's functional properties.

At 0.05 M concentration, the ZnO nanostructures appear as relatively small, uniformly distributed spherical particles. However, the packing density is lower, and the particles are loosely arranged with noticeable gaps between them. This indicates limited nucleation and growth, resulting in smaller crystallites and reduced surface interaction among particles.

In contrast, the 0.1 M thin film exhibits well-defined, densely packed spherical nanoparticles with clear grain boundaries. The particles are more uniform in size and show enhanced connectivity, forming a porous network structure. This morphology significantly increases the effective surface area and provides

more active sites for surface-related processes. The improved porosity and uniformity at this concentration are key factors contributing to superior performance in applications such as gas sensing. At a higher concentration of 0.15 M, the TEM image shows a more agglomerated and compact structure. The particles appear less distinct, with reduced clarity in grain boundaries due to excessive growth and coalescence. This leads to decreased porosity and reduced active surface area, which can negatively impact the material's efficiency. Overall, the 0.1 M ZnO thin film demonstrates an optimized balance between particle size, uniformity, and porosity, making it the most favorable condition for enhanced functional performance.

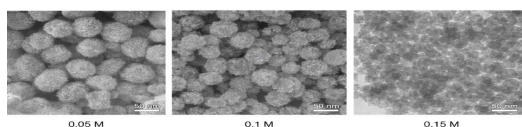


Figure 11: ZnO thin films at varying concentrations

Conclusions: Nanocrystalline ZnO thin films were successfully deposited at 0.05 M, 0.1 M, and 0.15 M concentrations using the spray pyrolysis technique. Their structural, morphological, optical, and gas sensing properties were systematically investigated. The crystallite size increased with molar concentration up to 0.1 M and then decreased at 0.15 M. FESEM analysis revealed uniformly distributed spherical particles with well-defined grain boundaries and enhanced porosity in the 0.1 M thin film, which contributes to improved gas sensing performance. Optical studies indicated that both transmittance and band gap decreased with increasing molar concentration. Gas sensing measurements, carried out using a custom-built setup, showed that the 0.1 M ZnO thin film exhibited the highest response toward NH_3 at 25 ppm. Additionally, this sample demonstrated faster response and recovery times compared to the 0.05 M and 0.15 M thin films. Overall, the enhanced sensing performance of the 0.1 M sample is attributed to its optimized morphology and increased surface activity.

References

1. Ganesh Kumar Mani. and John Bosco Balaguru Rayappan. (2014) "Selective detection of ammonia using spray pyrolysis deposited pure and nickel doped ZnO thin films" *Applied Surface Science*, 311, 405-412.
2. Rajendra S., Gauri R.Patil., Bhagwat N.Pawar and Rajaram S.Mane (2013) "Liquefied petroleum gas sensing properties of sprayed nanocrystalline zinc oxide thin films" *Sensors and Actuators A: Physical*, 189, 339-343.
3. Shewale. P.S., Patil. V.B., Shin.S.W., Kim. J.H., and Uplane. M.D (2013) "H₂S gas sensing properties of nanocrystalline Cu-doped ZnO thin films prepared by advanced spray pyrolysis" *Sensors and Actuators B: Chemical*, 186, 226-234.
4. Satish. S and Mulla. IS. (2011) "Effect of aluminium doping on structural and gas sensing properties of zinc oxide thin films deposited by spray pyrolysis" *Sensors and Actuators B: Chemical*, 156, 943-948.
5. Mariappan. R., Ponnuswamy. V. and Ragevendra. M. (2013) "Influence of molar concentration on the physical properties of nebulizer-sprayed ZnO thin films for ammonia gas sensor" *Materials Science in Semiconductor Processing*, 16(5), 1328-1335.
6. Oztas. M and Bedir.M (2008) "Thickness dependence of structural, electrical and optical properties of sprayed ZnO:Cu films" *Thin Solid Films*, 516, 1703-1709.
7. Patil. S.L., Chougule. M.A., Pawar. S.G., Sen., Shaswati. and Moholkar. A.V. (2011) "Fabrication of Polyaniline-ZnO Nanocomposite Gas Sensor" *Sensors and Transducers* 134, 120-131.
8. Pandiaturai. K., Mani. G.K., Shankar.P. and Rayappan. J.B.B. (2013) "ZnO nanospheres to nanorods - morphology transition via Fe-doping" *Superlattices & Microstructure*, 62, 39-46.
9. Timmer. B., Olthuis. W. and Van den Berg. A. (2005) "Ammonia sensors and their applications-a review" *Sensors and Actuators B: Chemical*, 107, 666-677.
10. Torres Delgado. G., Zúñiga Romero. C.I., Mayén Hernández. S.A., Castanedo Pérez. R. and Zelaya Angel. O. (2009) "Optical and structural properties of the sol-gel-prepared ZnO thin film and their effect on the photocatalytic activity" *Solar Energy Materials & Solar Cells* 93, 55-59.
11. Tesfamichael. T., Cetin. C., Piloto. C., Arita. M. and Bell. J. (2015) "The effect of pressure and W-doping on the properties of ZnO thin films for NO₂ gas sensing" *Applied Surface Science*, 357, 728-734.