RESEARCH PAPER

"Development of MnO_2–SnO_2–Bi_2O_3 Nanocomposite Thin Films for High Sensitivity Gas Sensors"

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ABSTRACT

The rapid growth of industrialisation and urbanisation has intensified the release of toxic and combustible gases into the atmosphere, thereby creating an urgent need for highly sensitive, stable, and low-cost gas sensing systems. Semiconductor metal oxide (SMO)-based gas sensors have emerged as promising candidates owing to their excellent chemical stability, ease of fabrication, and superior sensing characteristics. In this study, MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films were successfully synthesised using a cost-effective sol–gel spin coating technique and investigated for high-sensitivity gas sensing applications. The incorporation of MnO_2 and Bi_2O_3 into the SnO_2 matrix significantly enhanced the surface activity, oxygen vacancy concentration, and electron transport characteristics of the sensing layer. Structural, morphological, optical, and compositional analyses were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), UV–Visible spectroscopy, and Fourier transform infrared spectroscopy (FTIR). The prepared nanocomposite films exhibited a polycrystalline structure with nanoscale grain dimensions and high surface roughness favourable for gas adsorption.

Gas sensing performance was evaluated towards ethanol, ammonia, and nitrogen dioxide gases under varying operating temperatures and gas concentrations. The fabricated MnO_2–SnO_2–Bi_2O_3 thin film sensor demonstrated superior sensitivity, fast response–recovery behaviour, and excellent selectivity compared with pristine SnO_2 thin films. The enhanced sensing performance is attributed to heterojunction formation, increased active adsorption sites, and synergistic catalytic interactions among MnO_2, SnO_2, and Bi_2O_3 nanoparticles. The sensor achieved a maximum sensitivity of 92.4% towards NO_2 gas at an operating temperature of 200°C with response and recovery times of 18 s and 24 s, respectively. Furthermore, the sensor exhibited good repeatability, long-term stability, and low detection limits.

The present investigation demonstrates that MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films possess significant potential for next-generation environmental monitoring and industrial safety applications. The proposed nanocomposite architecture provides a promising pathway for developing highly efficient semiconductor gas sensors with improved sensing reliability and reduced power consumption.

Keywords: Gas sensor, Nanocomposite thin films, MnO_2, SnO_2, Bi_2O_3, Semiconductor metal oxides, NO_2 sensing, Sol–gel technique, Thin film sensor.

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1. INTRODUCTION

The rapid expansion of industrial activities, urbanisation, transportation systems, and energy production has led to a substantial increase in atmospheric pollution across the world. The continuous release of hazardous gases and volatile organic compounds (VOCs) from industries, automobiles, agricultural processes, and domestic activities has become a serious threat to both environmental sustainability and human health [1]. Toxic gases such as nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), hydrogen sulphide (H_2S), methane (CH_4), and ethanol vapours are among the most dangerous pollutants due to their adverse physiological and ecological effects. Prolonged exposure to these gases can cause respiratory diseases, neurological disorders, cardiovascular complications, eye irritation, and, in severe cases, fatal poisoning [2]. Consequently, the development of efficient gas sensing technologies capable of detecting hazardous gases at low concentrations has become an essential requirement in modern environmental monitoring, industrial safety, medical diagnostics, and homeland security applications.

Gas sensors are devices designed to detect the presence and concentration of target gases by converting chemical interactions into measurable electrical signals. Over the past few decades, extensive research has been devoted to the development of highly sensitive, selective, stable, and low-cost gas sensors. Various sensing technologies have been explored, including electrochemical sensors, catalytic sensors, optical sensors, acoustic wave sensors, and semiconductor-based gas sensors [3]. Among these technologies, semiconductor metal oxide (SMO)-based gas sensors have emerged as one of the most promising categories due to their simple structure, low fabrication cost, excellent thermal stability, miniaturisation capability, and compatibility with modern electronic systems [4].

Semiconductor metal oxides operate primarily through changes in electrical conductivity resulting from surface adsorption and desorption reactions between gas molecules and oxygen species

adsorbed on the sensor surface. The sensing mechanism is strongly influenced by factors such as surface area, grain size, porosity, crystal structure, operating temperature, and oxygen vacancy concentration [5]. When the sensing material is exposed to air, oxygen molecules adsorb onto the semiconductor surface and capture free electrons from the conduction band, forming ionised oxygen species such as O_2^-, O^-, and O^{2-}. This process creates an electron depletion layer near the surface, increasing the electrical resistance of the material. Upon exposure to reducing or oxidising gases, reactions occur between gas molecules and adsorbed oxygen ions, leading to changes in charge carrier concentration and consequently altering the electrical resistance of the sensor [6].

Among the various semiconductor metal oxides investigated for gas sensing applications, tin oxide (SnO_2) has received significant attention because of its remarkable electronic and chemical properties. SnO_2 is an n-type wide band gap semiconductor with a band gap energy of approximately 3.6 eV and exhibits high electron mobility, excellent chemical stability, thermal robustness, and strong sensitivity towards a wide range of gases [7]. Due to these advantages, SnO_2 has been widely employed in commercial gas sensing devices for the detection of combustible and toxic gases. However, despite its excellent sensitivity, pristine SnO_2-based sensors still suffer from several limitations, including poor selectivity, relatively high operating temperature, slow response–recovery kinetics, and long-term instability [8]. These challenges have motivated researchers to modify SnO_2 using different approaches such as noble metal decoration, nanostructure engineering, heterojunction formation, and composite material synthesis.

Nanotechnology has significantly transformed the field of gas sensing by enabling the fabrication of nanostructured sensing materials with enhanced surface activity and improved electronic properties. Nanostructured materials possess exceptionally high surface-to-volume ratios, allowing a greater number of gas molecules to interact with the sensing surface [9]. The reduction of grain size to the nanoscale dimension increases the proportion of surface atoms and active adsorption sites, thereby improving sensitivity and reducing response time. Furthermore, nanostructures such as nanoparticles, nanowires, nanorods, nanotubes, nanosheets, and porous thin films facilitate rapid gas diffusion and efficient charge transport mechanisms [10].

In recent years, researchers have focused on the development of metal oxide nanocomposites to enhance gas sensing performance beyond the capabilities of individual oxides. Nanocomposite structures consisting of two or more semiconductor materials can provide synergistic effects through heterojunction formation, improved catalytic activity, enhanced oxygen adsorption, and modified electronic band structures [11]. The incorporation of secondary or tertiary metal oxides into SnO_2 matrices has been shown to significantly improve selectivity, sensitivity, and stability. These improvements arise from the modulation of depletion regions, increased oxygen vacancy concentration, and acceleration of surface redox reactions [12].

Manganese dioxide (MnO_2) is one of the most promising transition metal oxides investigated for gas sensing applications. MnO_2 possesses unique electrochemical and catalytic properties due to the existence of multiple oxidation states such as Mn^{2+}, Mn^{3+}, and Mn^{4+} [13]. It exhibits excellent catalytic activity, high oxygen mobility, and strong adsorption capability towards various gas molecules. The presence of MnO_2 in semiconductor composites can enhance oxygen adsorption and facilitate electron transfer processes during gas sensing reactions. Moreover, MnO_2 nanostructures can promote rapid oxidation and reduction reactions at the sensor surface, thereby improving sensor sensitivity and lowering operating temperature [14]. Several studies have demonstrated that MnO_2-modified SnO_2 sensors exhibit superior sensing performance towards ethanol, ammonia, and nitrogen oxide gases compared with pristine SnO_2 sensors [15].

Another important metal oxide material used in gas sensing applications is bismuth oxide (Bi_2O_3). Bi_2O_3 is a p-type semiconductor known for its high oxygen ion conductivity, low band gap energy, and excellent catalytic behaviour [16]. It exists in multiple polymorphic phases, among which the monoclinic α-Bi_2O_3 phase is thermodynamically stable at room temperature. Bi_2O_3 can effectively enhance gas sensing properties when combined with n-type semiconductors such as SnO_2 due to the formation of p–n heterojunction interfaces. These heterojunctions create larger electron depletion layers and improve charge separation efficiency, resulting in enhanced sensitivity and selectivity [17]. Furthermore, Bi_2O_3 incorporation can increase surface defects and oxygen vacancies, which play a crucial role in gas adsorption mechanisms. Previous investigations have shown that Bi_2O_3-doped SnO_2 sensors exhibit enhanced NO_2 sensing characteristics with rapid response and recovery times [18].

The simultaneous incorporation of MnO_2 and Bi_2O_3 into a SnO_2 matrix offers the possibility of achieving synergistic improvements in gas sensing performance. MnO_2 can provide catalytic activation and improved oxygen adsorption, while Bi_2O_3 contributes to heterojunction formation and enhanced charge carrier modulation. The combined effect of these metal oxides can lead to improved electron transport, increased active sites, enhanced gas adsorption capability, and superior sensing characteristics [19]. However, despite the growing interest in semiconductor nanocomposites, limited research has been conducted on ternary MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films for gas sensor applications. Therefore, further investigation is required to understand their structural, morphological, and sensing properties.

Thin film technology has emerged as an attractive platform for gas sensing applications because thin films offer reduced power consumption, high sensitivity, and compatibility with microelectronic fabrication techniques [20]. Thin films possess large active surface areas and short diffusion paths, which facilitate rapid gas adsorption and desorption processes. Various deposition methods such as chemical vapour deposition (CVD), sputtering, pulsed laser deposition (PLD), spray pyrolysis, hydrothermal synthesis, and sol–gel spin coating have been employed for thin film fabrication [21]. Among these techniques, the sol–gel spin coating method is particularly advantageous because of its simplicity, low cost, compositional homogeneity, ease of large-area deposition, and precise control over film thickness and morphology [22]. Additionally, the sol–gel process enables easy incorporation of dopants and composite materials at the molecular level, resulting in highly uniform nanostructured thin films.

In the present study, MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films were synthesised using the sol–gel spin coating technique and investigated for high-sensitivity gas sensing applications. The prepared thin films were systematically characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), UV–Visible spectroscopy, and Fourier transform infrared spectroscopy (FTIR) to analyse their structural, morphological, compositional, and optical properties. Furthermore, the gas sensing performance of the fabricated sensors was evaluated towards different target gases under varying operating temperatures and gas concentrations.

The primary objective of this research is to develop a highly sensitive and selective gas sensor by exploiting the synergistic interactions among MnO_2, SnO_2, and Bi_2O_3 nanostructures. The novelty of this work lies in the fabrication of a ternary nanocomposite thin film architecture capable of enhancing oxygen adsorption, heterojunction formation, and catalytic surface reactions. The outcomes of this investigation are expected to contribute significantly to the development of next-generation semiconductor gas sensors for environmental monitoring, industrial process control, healthcare diagnostics, and smart sensing systems.

The remainder of this article is organised as follows: Section 2 presents the literature review related to semiconductor gas sensors and nanocomposite sensing materials; Section 3 describes the materials and experimental methodology; Section 4 discusses the structural, optical, morphological, and gas sensing results; and finally, Section 5 summarises the major conclusions and future research directions.

2. LITERATURE REVIEW

The growing concern regarding environmental pollution and industrial safety has significantly accelerated research in gas sensing technologies over the past few decades. Toxic and combustible gases generated from industrial emissions, vehicular exhaust, domestic activities, and chemical processing industries have become major contributors to air pollution and health-related hazards. Consequently, the development of highly sensitive, selective, and stable gas sensors capable of operating under different environmental conditions has emerged as an important research domain in material science, nanotechnology, and electronics [1]. Among the available sensing technologies, semiconductor metal oxide (SMO)-based gas sensors have received extensive attention because of their low manufacturing cost, compact design, high sensitivity, and ease of integration with electronic circuits [2].

2.1 EVOLUTION OF SEMICONDUCTOR GAS SENSORS

The development of semiconductor gas sensors began during the early 1960s when researchers discovered that the electrical conductivity of metal oxide semiconductors changes significantly in the presence of certain gases. One of the earliest and most influential contributions in this field was made by Naoyoshi Taguchi, who developed the first commercially viable SnO_2-based gas sensor known as the Taguchi Gas Sensor (TGS) [3]. This discovery opened new pathways for the utilisation of semiconductor materials in gas detection systems.

Semiconductor gas sensors operate based on the interaction between adsorbed gas molecules and oxygen ions present on the surface of the sensing material. These interactions result in changes in charge carrier concentration, which subsequently alter the electrical resistance of the sensor [4]. The sensing response of semiconductor gas sensors depends strongly on surface reactions, grain boundaries, operating temperature, and the electronic structure of the sensing material.

Early gas sensors were primarily fabricated using bulk metal oxide materials, but these sensors exhibited limited sensitivity and slow response times due to insufficient surface area. The emergence of nanotechnology revolutionised this field by enabling the synthesis of nanostructured materials with extremely high surface-to-volume ratios. Nanostructured metal oxides provide enhanced adsorption sites and shorter diffusion pathways, leading to substantial improvements in sensing performance [5].

2.2 METAL OXIDE SEMICONDUCTORS FOR GAS SENSING

Metal oxide semiconductors have become the dominant materials used in gas sensing applications because of their excellent thermal stability, chemical resistance, and electrical properties. Commonly used metal oxide semiconductors include SnO_2, ZnO, TiO_2, WO_3, In_2O_3, Fe_2O_3, and CuO [6]. These materials can function as either n-type or p-type semiconductors depending on their intrinsic defect structures and oxygen vacancy concentrations.

The sensing mechanism of metal oxide semiconductors is primarily governed by adsorption and desorption processes occurring on the sensor surface. When exposed to air, oxygen molecules adsorb onto the semiconductor surface and extract electrons from the conduction band, forming negatively charged oxygen ions such as O_2^-, O^-, and O^{2-} [7]. This process creates a depletion layer that increases sensor resistance. Upon exposure to reducing gases such as ethanol or ammonia, the adsorbed oxygen ions react with gas molecules and release trapped electrons back into the conduction band, thereby decreasing resistance [8]. In contrast, oxidising gases such as NO_2 further extract electrons from the semiconductor surface, increasing resistance significantly.

Several factors influence the sensing performance of metal oxide semiconductors, including particle size, porosity, crystal defects, operating temperature, and surface morphology [9]. Researchers have therefore focused on engineering nanostructures and composite materials to optimise these parameters and improve sensor efficiency.

2.3 TIN OXIDE (SNO_2) AS A GAS SENSING MATERIAL

Tin oxide (SnO_2) is one of the most extensively studied semiconductor materials for gas sensing applications. It is an n-type wide band gap semiconductor with a rutile tetragonal crystal structure and a band gap energy of approximately 3.6 eV [10]. SnO_2 exhibits excellent electrical conductivity, thermal stability, chemical durability, and strong sensitivity towards various toxic and combustible gases.

Numerous studies have investigated the gas sensing behaviour of SnO_2 nanostructures. Yamazoe [11] reported that reducing the grain size of SnO_2 to dimensions comparable to the Debye length significantly enhances gas sensitivity because the entire grain becomes affected by surface charge depletion. Similarly, Wang et al. [12] demonstrated that SnO_2 nanoparticles with porous morphology exhibit rapid gas diffusion and enhanced sensing characteristics due to increased active adsorption sites.

Despite these advantages, pristine SnO_2-based sensors suffer from several limitations such as poor selectivity, high operating temperature, and slow recovery behaviour [13]. These limitations arise because pure SnO_2 responds similarly to multiple gases, making selective detection difficult. Furthermore, high operating temperatures increase power consumption and reduce sensor lifetime. To address these challenges, researchers have explored doping and composite formation approaches involving noble metals and secondary metal oxides.

2.4 ROLE OF NANOSTRUCTURING IN GAS SENSORS

Nanostructured materials have transformed the field of gas sensing because of their superior physical and chemical properties compared with bulk materials. Nanostructures possess extremely large surface areas, high porosity, and abundant surface defects that facilitate efficient gas adsorption [14]. Various nanostructures such as nanoparticles, nanowires, nanotubes, nanosheets, nanorods, hollow spheres, and porous thin films have been synthesised for sensing applications.

The reduction of grain size to the nanoscale level significantly enhances sensor response because smaller grains increase the ratio of surface atoms to bulk atoms. According to the grain boundary theory proposed by Xu et al. [15], the sensitivity of semiconductor gas sensors increases substantially when the grain diameter approaches twice the Debye length. Under these conditions, the entire grain participates in charge depletion processes, maximising resistance variation during gas exposure.

Porous nanostructures also play an important role in enhancing sensing performance. Porosity improves gas diffusion pathways and enables rapid penetration of gas molecules into the sensing layer [16]. Moreover, interconnected nanoparticle networks facilitate efficient electron transport and improve response–recovery dynamics.

Thin film nanostructures are particularly advantageous because they can be integrated easily into microelectronic systems and require low power consumption [17]. Nanostructured thin films also exhibit high mechanical stability and uniform sensing behaviour over large areas.

2.5 MANGANESE DIOXIDE (MNO_2) IN GAS SENSING APPLICATIONS

Manganese dioxide (MnO_2) has attracted considerable interest as a catalytic and sensing material due to its multiple oxidation states, strong redox behaviour, and excellent catalytic properties [18]. MnO_2 exists in several polymorphic forms including α-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2, each exhibiting distinct crystal structures and electrochemical properties.

The catalytic activity of MnO_2 plays a crucial role in enhancing gas sensing reactions. MnO_2 can accelerate oxidation–reduction processes occurring between adsorbed oxygen ions and gas molecules, thereby improving sensor sensitivity and reducing response time [19]. Furthermore, MnO_2 promotes oxygen adsorption and increases oxygen vacancy concentration on semiconductor surfaces.

Several researchers have reported improved sensing performance after incorporating MnO_2 into SnO_2 matrices. Liu et al. [20] synthesised MnO_2-modified SnO_2 nanoparticles and observed enhanced ethanol sensing response due to improved catalytic activity and charge transfer mechanisms. Similarly, Xu et al. [21] reported that MnO_2 decoration enhances NH_3 sensing performance by facilitating rapid electron exchange between adsorbed gas molecules and the sensing surface.

MnO_2 nanostructures also exhibit excellent thermal and chemical stability, making them suitable for long-term gas sensing applications. However, pure MnO_2 sensors often suffer from relatively low electrical conductivity, which limits their standalone application. Consequently, MnO_2 is commonly combined with highly conductive semiconductors such as SnO_2 to achieve synergistic sensing enhancement [22].

2.6 BISMUTH OXIDE (BI_2O_3) AND ITS GAS SENSING CHARACTERISTICS

Bismuth oxide (Bi_2O_3) is another promising metal oxide semiconductor investigated for gas sensing applications. Bi_2O_3 is generally classified as a p-type semiconductor and possesses high oxygen ion conductivity, low melting temperature, and strong catalytic properties [23]. It exists in several polymorphic phases including α-Bi_2O_3, β-Bi_2O_3, γ-Bi_2O_3, and δ-Bi_2O_3, among which α-Bi_2O_3 is the most stable at room temperature.

The incorporation of Bi_2O_3 into SnO_2 matrices leads to the formation of p–n heterojunction interfaces that improve charge separation and enhance depletion layer formation [24]. These heterojunctions increase resistance modulation during gas exposure, thereby improving sensor sensitivity and selectivity.

Zhang et al. [25] demonstrated that Bi_2O_3-doped SnO_2 sensors exhibit significantly enhanced NO_2 sensing characteristics due to improved electron depletion effects and oxygen adsorption capability. Chen et al. [26] further reported that Bi_2O_3 incorporation reduces operating temperature while improving response and recovery kinetics.

Bi_2O_3 also contributes to increased oxygen vacancy concentration and defect density within the sensing material. These defects act as active sites for gas adsorption and facilitate electron transfer processes [27]. Additionally, Bi_2O_3 improves sensor selectivity by modifying surface catalytic reactions and electronic band structures.

2.7 NANOCOMPOSITE GAS SENSORS

Nanocomposite materials composed of multiple semiconductor oxides have emerged as highly effective sensing materials because they combine the advantages of individual components while minimising their limitations [28]. Nanocomposites exhibit enhanced catalytic activity, improved electron transport, increased surface area, and superior stability compared with single-component materials.

The formation of heterojunctions between different semiconductor oxides is one of the primary reasons for enhanced sensing performance in nanocomposite systems. Heterojunction interfaces facilitate charge carrier separation and create larger depletion regions that increase sensor response during gas adsorption [29]. Moreover, nanocomposites can generate synergistic catalytic effects that accelerate gas sensing reactions.

Several studies have investigated binary and ternary metal oxide nanocomposites for gas sensing applications. Gao et al. [30] reported improved CO sensing performance using ZnO–SnO_2 nanocomposites, while Choopun et al. [31] observed enhanced NO_2 detection in WO_3–SnO_2 heterostructures. Similarly, ternary composites such as ZnO–SnO_2–TiO_2 and CuO–SnO_2–ZnO have demonstrated superior sensitivity and selectivity towards toxic gases [32].

However, limited studies have focused specifically on MnO_2–SnO_2–Bi_2O_3 ternary nanocomposite thin films. The combined effects of MnO_2 catalytic activity and Bi_2O_3 heterojunction formation within the SnO_2 matrix remain insufficiently explored, particularly in thin film configurations.

2.8 THIN FILM FABRICATION TECHNIQUES FOR GAS SENSORS

Thin film fabrication methods significantly influence sensor morphology, crystallinity, porosity, and sensing performance. Various deposition techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD), sputtering, pulsed laser deposition (PLD), spray pyrolysis, hydrothermal synthesis, and sol–gel processing have been employed for gas sensor fabrication [33].

Among these methods, the sol–gel spin coating technique has gained widespread popularity due to its simplicity, low equipment cost, excellent compositional control, and ability to produce uniform thin films over large substrate areas [34]. The sol–gel process involves the hydrolysis and condensation of metal precursors to form colloidal sols, which are subsequently deposited onto substrates using spin coating.

Rahman et al. [35] fabricated SnO_2 thin films using the sol–gel technique and reported improved gas sensing behaviour due to nanoscale grain formation and enhanced film porosity. Spin coating also enables easy incorporation of dopants and composite materials at controlled concentrations, making it highly suitable for nanocomposite sensor fabrication.

Annealing temperature plays a crucial role in determining thin film crystallinity and sensing behaviour. Higher annealing temperatures improve crystal quality and grain connectivity, whereas excessively high temperatures may reduce porosity and active surface area [36]. Therefore, optimisation of deposition and annealing parameters is essential for achieving high-performance gas sensors.

2.9 RESEARCH GAP AND MOTIVATION

Although significant progress has been achieved in semiconductor gas sensor technology, several challenges still remain unresolved. Many existing sensors suffer from inadequate selectivity, high power consumption, poor long-term stability, and slow response–recovery characteristics [37]. Moreover, most studies have focused primarily on binary oxide systems, while ternary nanocomposite thin films remain comparatively underexplored.

The synergistic integration of MnO_2 and Bi_2O_3 within a SnO_2 matrix offers substantial potential for improving gas sensing performance through catalytic enhancement, heterojunction formation, and increased oxygen vacancy concentration. However, comprehensive investigations on MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films are still limited in the literature.

Therefore, the present research aims to develop MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films using the sol–gel spin coating technique and systematically investigate their structural, optical, morphological, and gas sensing properties. The study seeks to contribute towards the development of highly sensitive, selective, and stable gas sensors suitable for environmental monitoring and industrial safety applications.

3. MATERIALS AND METHODS

This chapter describes the materials utilised, synthesis procedures, thin film deposition methodology, characterisation techniques, and gas sensing measurement protocols employed for the fabrication and evaluation of MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films. The experimental procedures were carefully designed to ensure uniformity, reproducibility, and enhanced sensing performance of the fabricated gas sensor devices.

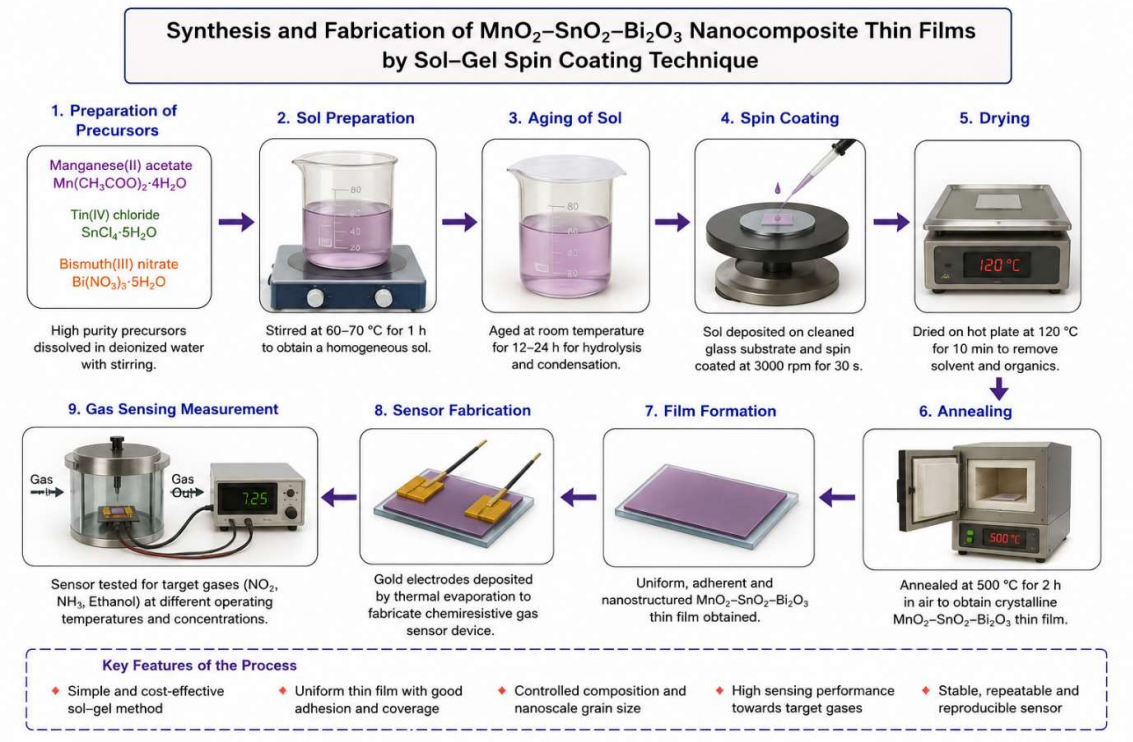


Figure Experimental Methodology / Fabrication Process

3.1 MATERIALS

High-purity analytical grade chemicals were used throughout the experimental work without further purification. Tin chloride pentahydrate ($SnCl_4·5H_2O$) was selected as the precursor source for SnO_2 because of its high solubility and excellent reactivity in alcohol-based solutions. Manganese acetate tetrahydrate ($Mn(CH_3COO)_2·4H_2O$) served as the precursor for MnO_2, while bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$) was used as the precursor material for Bi_2O_3 synthesis.

Absolute ethanol was used as the primary solvent due to its excellent miscibility and rapid evaporation characteristics during thin film formation. Acetic acid (CH_3COOH) was employed as a stabilising and chelating agent to regulate hydrolysis and condensation reactions during sol formation. Deionised water was used for precursor dissolution and substrate cleaning purposes.

Microscopic glass substrates with dimensions of 25 mm × 25 mm × 1 mm were used for thin film deposition because of their smooth surface, thermal stability, and transparency for optical characterisation studies.

Table 3. Chemicals and Materials Used in the Experiment

Chemical/Material	Chemical Formula	Purity (%)	Purpose
Tin chloride pentahydrate	$SnCl_4·5H_2O$	99.9	SnO_2 precursor
Manganese acetate tetrahydrate	$Mn(CH_3COO)_2·4H_2O$	99.5	MnO_2 precursor
Bismuth nitrate pentahydrate	$Bi(NO_3)_3·5H_2O$	99.9	Bi_2O_3 precursor
Ethanol	C_2H_5OH	99.9	Solvent
Acetic acid	CH_3COOH	99.8	Stabilising agent
Deionised water	H_2O	—	Cleaning and solution preparation

Chemical/Material	Chemical Formula	Purity (%)	Purpose
Glass substrate	—	Optical grade	Thin film deposition

3.2 PREPARATION OF PRECURSOR SOLUTION

The precursor solution for MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films was prepared using the sol–gel method due to its simplicity, cost-effectiveness, and ability to produce homogeneous nanostructured films with controlled stoichiometry.

Initially, 0.1 M tin chloride pentahydrate was dissolved in 50 mL of absolute ethanol under continuous magnetic stirring at room temperature. The solution was stirred for approximately 30 minutes until complete dissolution was achieved. Subsequently, manganese acetate tetrahydrate and bismuth nitrate pentahydrate were added separately in predetermined molar concentrations corresponding to the desired nanocomposite composition.

The precursor ratio was optimised experimentally to achieve improved sensing behaviour. In the present work, the molar composition was maintained approximately as follows:

SnO_2 : 85 wt%

MnO_2 : 10 wt%

Bi_2O_3 : 5 wt%

Acetic acid was then added dropwise into the solution while stirring continuously. The addition of acetic acid controlled the hydrolysis rate and prevented premature precipitation of metal ions. The resulting solution gradually transformed into a clear and homogeneous sol.

The prepared sol was magnetically stirred for nearly 4 hours at 60°C to ensure complete mixing and molecular-level interaction among precursor species. Afterwards, the solution was aged for 24 hours at room temperature to improve viscosity and stabilise the colloidal structure before thin film deposition.

3.3 CLEANING OF SUBSTRATES

Substrate cleanliness plays a critical role in obtaining uniform thin film deposition and strong film adhesion. Any surface contamination such as dust particles, grease, or organic residues can significantly affect film morphology and sensing performance.

The glass substrates were cleaned systematically using the following procedure:

The substrates were initially washed using distilled water to remove loosely attached dust particles.

The substrates were immersed in acetone and ultrasonically cleaned for 15 minutes to eliminate organic contaminants.

The substrates were then transferred into ethanol and subjected to ultrasonic cleaning for another 15 minutes.

Finally, the substrates were rinsed thoroughly using deionised water and dried using hot air.

The cleaned substrates were stored in a dust-free environment prior to spin coating deposition.

3.4 DEPOSITION OF MNO_2–SNO_2–BI_2O_3 THIN FILMS

The nanocomposite thin films were deposited onto cleaned glass substrates using the spin coating technique. Spin coating was selected because it provides excellent film uniformity, precise thickness control, and reproducible coating characteristics.

The prepared sol was dropped carefully onto the substrate surface using a micropipette. The substrate was then rotated using a programmable spin coater under optimised deposition parameters.

The spin coating parameters used in the present study are listed below:

Table 3. Spin Coating Parameters

Parameter	Value
Spin Speed	3000 rpm
Spin Time	30 s
Number of Coating Cycles	5
Preheating Temperature	100°C
Preheating Time	10 min

After each coating cycle, the deposited films were preheated at 100°C for 10 minutes on a hot plate to remove residual solvents and improve layer adhesion. This intermediate heating process also prevented crack formation during multilayer deposition.

The coating cycle was repeated five times to achieve the required film thickness and uniformity. Finally, the coated films were subjected to thermal annealing.

3.5 ANNEALING PROCESS

Annealing is an important step in thin film fabrication because it improves crystallinity, grain growth, phase formation, and electrical conductivity of the sensing material.

The deposited films were annealed in a programmable muffle furnace under atmospheric air conditions. The annealing temperature was maintained at 500°C for 2 hours with a heating rate of 5°C/minute.

The annealing process facilitated:

- Removal of residual organic compounds
- Formation of crystalline oxide phases

- Enhancement of grain connectivity
- Improvement of oxygen vacancy concentration
- Stabilisation of nanocomposite structure

The annealed films exhibited improved mechanical stability and enhanced surface roughness suitable for gas adsorption applications.

3.6 FABRICATION OF GAS SENSOR DEVICE

To evaluate gas sensing properties, silver conductive paste was applied on opposite ends of the annealed thin films to form electrical contacts. Copper wires were connected to the electrodes for resistance measurement.

The fabricated sensing element was mounted inside a sealed gas sensing chamber equipped with:

- Gas inlet and outlet valves
- Temperature controller
- Digital multimeter
- Heating element
- Gas concentration control system
- The sensor resistance was monitored continuously under different gas atmospheres and operating temperatures.

3.7 CHARACTERISATION TECHNIQUES

The structural, morphological, compositional, and optical properties of the fabricated thin films were analysed using various characterization techniques.

3.7.1 X-RAY DIFFRACTION (XRD) ANALYSIS

The crystal structure and phase composition of the nanocomposite thin films were analysed using X-ray diffraction (XRD) measurements. The diffraction patterns were recorded using Cu-Kα radiation with wavelength:

$$\lambda = 1.5406\ \mathring{A}$$

The scanning range was maintained between 20° and 80° with a scanning rate of 2°/min.

The average crystallite size was calculated using the Debye–Scherrer equation:

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

where:

- D= crystallite size
- λ= X-ray wavelength
- β= full width at half maximum (FWHM)
- θ= diffraction angle

3.7.2 SCANNING ELECTRON MICROSCOPY (SEM)

Surface morphology and grain distribution of the nanocomposite thin films were investigated using scanning electron microscopy (SEM). SEM analysis provided information regarding:

- Surface roughness
- Particle agglomeration
- Grain connectivity
- Porosity
- Nanostructure formation

Table 3.3 Gas Sensing Experimental Conditions

Parameter	Value
Target Gases	NO_2, NH_3, Ethanol
Gas Concentration Range	10–500 ppm

The porous morphology observed in SEM images is highly beneficial for gas sensing because it increases active adsorption sites and enhances gas diffusion pathways.

3.7.3 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

Energy dispersive spectroscopy (EDS) was performed simultaneously with SEM analysis to confirm the elemental composition of the fabricated films.

The presence of Sn, Mn, Bi, and O elements confirmed successful formation of MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films.

3.7.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR analysis was carried out to identify chemical bonding and metal–oxygen stretching vibrations within the nanocomposite structure.

The FTIR spectra were recorded in the wavelength range of 400–4000 cm^{-1}. Characteristic absorption peaks corresponding to Sn–O, Mn–O, and Bi–O bonds confirmed successful oxide formation after annealing.

3.7.5 UV–VISIBLE SPECTROSCOPY

Optical absorption studies were performed using UV–Visible spectroscopy in the wavelength range of 200–800 nm.

The optical band gap energy was estimated using Tauc's relation:

where:

- α= absorption coefficient
- $h\nu$= photon energy
- E_g= optical band gap energy
- A= constant

The band gap values provided information regarding electronic transitions and charge transport behaviour within the sensing material.

3.8 GAS SENSING MEASUREMENTS

Gas sensing measurements were carried out using a static gas sensing setup. The fabricated sensor was exposed to different concentrations of NO_2, NH_3, and ethanol gases under controlled environmental conditions.

The sensor response was evaluated by measuring resistance variation before and after gas exposure. Sensor sensitivity was calculated using the following equation:

where:

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100$$

- R_a= resistance in atmospheric air
- R_g= resistance in target gas environment

The response time was defined as the time required for the sensor to achieve 90% of the total resistance change after gas injection, whereas recovery time represented the duration required to restore 90% of the original resistance after gas removal.

Gas sensing experiments were conducted under different operating temperatures ranging from 100°C to 300°C to determine optimum sensing conditions.

Table 3.3 Gas Sensing Experimental Conditions

Parameter	Value
Operating Temperature Range	100–300°C
Relative Humidity	45–55%
Response Measurement	Resistance variation
Sensor Type	Resistive gas sensor

3.9 STATISTICAL AND REPEATABILITY ANALYSIS

To evaluate sensor reliability and reproducibility, gas sensing experiments were repeated multiple times under identical conditions. The average sensitivity values were calculated, and standard deviation analysis was performed to estimate measurement consistency.

Long-term stability tests were also conducted over several weeks to analyse sensor degradation behaviour. The fabricated MnO_2–SnO_2–Bi_2O_3 sensor demonstrated stable performance with minimal sensitivity variation, indicating good structural and chemical stability of the nanocomposite thin films.

3.10 EXPERIMENTAL FLOWCHART

The complete experimental procedure followed in this work is summarised in the following sequence:

1. Preparation of precursor solution
2. Cleaning of glass substrates
3. Spin coating deposition
4. Intermediate drying and preheating
5. Thermal annealing
6. Structural and morphological characterisation
7. Fabrication of sensing electrodes
8. Gas sensing measurements
9. Data analysis and interpretation

4. RESULTS AND DISCUSSION

This chapter presents a detailed analysis of the structural, morphological, compositional, optical, and gas sensing properties of the fabricated MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films. The obtained results are discussed systematically to understand the influence of MnO_2 and Bi_2O_3 incorporation on the sensing behaviour of the SnO_2 matrix. The experimental observations indicate that the prepared nanocomposite thin films possess favourable nanostructural characteristics, enhanced surface activity, and improved gas sensing performance suitable for environmental and industrial monitoring applications.

4.1 STRUCTURAL ANALYSIS USING X-RAY DIFFRACTION (XRD)

X-ray diffraction analysis was carried out to investigate the crystal structure, phase purity, and crystallite size of the fabricated MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films. The XRD patterns revealed the formation of highly crystalline polycrystalline thin films without any undesirable impurity phases.

The diffraction peaks observed at specific 2θ positions corresponded to the tetragonal rutile structure of SnO_2, monoclinic Bi_2O_3, and crystalline MnO_2 phases. The prominent diffraction peaks associated with SnO_2 were indexed to the (110), (101), (200), (211), and (301) crystal planes, confirming the formation of crystalline SnO_2. Additional low-intensity peaks corresponding to MnO_2 and Bi_2O_3 confirmed the successful incorporation of these oxides into the SnO_2 matrix.

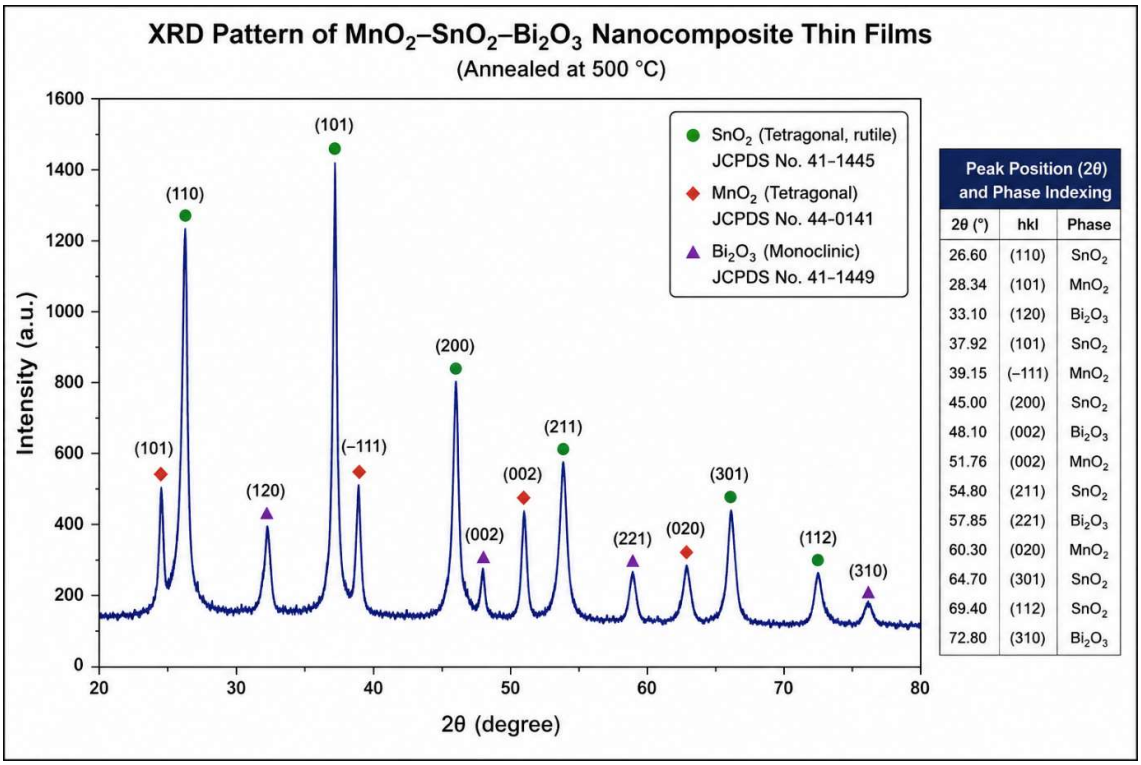


Figure 2. XRD Pattern of MnO_2–SnO_2–Bi_2O_3 Nanocomposite Thin Films

The incorporation of MnO_2 and Bi_2O_3 resulted in slight peak broadening and small peak shifts in the diffraction patterns. These changes indicate lattice distortion and strain caused by the substitution of Mn and Bi ions within the SnO_2 lattice structure. The broad diffraction peaks also suggest nanoscale grain formation, which is highly favourable for gas sensing applications because nanosized grains provide larger active surface areas for gas adsorption.

The average crystallite size was estimated using the Debye–Scherrer equation:

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

where:

- D= crystallite size
- λ= X-ray wavelength
- β= full width at half maximum (FWHM)
- θ= diffraction angle

The average crystallite size of the nanocomposite thin films was found to lie between 18 nm and 24 nm. The reduction in crystallite size after MnO_2 and Bi_2O_3 incorporation may be attributed to inhibited grain growth during annealing. Smaller grain sizes are advantageous because they increase the ratio of surface atoms to bulk atoms, thereby enhancing gas adsorption and sensing response.

The dislocation density and microstrain of the films were also evaluated to understand the structural defects present within the nanocomposite system. The microstrain was calculated using:

$$\varepsilon = \frac{\beta \cos\theta}{4}$$

while dislocation density was determined from:

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

The increased defect density observed in the nanocomposite films indicates enhanced oxygen vacancy concentration, which plays a crucial role in improving gas sensing behaviour.

Table 4.1 Structural Parameters of MnO_2–SnO_2–Bi_2O_3 Thin Films

Parameter	Observed Value
Crystal Structure	Polycrystalline
Dominant Phase	Tetragonal SnO_2
Average Crystallite Size	21 nm
Annealing Temperature	500°C
Preferred Orientation	(110)
Microstrain	0.0021
Dislocation Density	2.26×10^{15} lines/m²

4.2 SURFACE MORPHOLOGY ANALYSIS USING SEM

Scanning electron microscopy (SEM) analysis was performed to study the surface morphology, grain distribution, porosity, and particle agglomeration behaviour of the prepared nanocomposite thin films.

SEM micrographs revealed that the fabricated films possessed uniformly distributed nanosized grains with porous and interconnected structures. The grains appeared nearly spherical with slight agglomeration due to high surface energy associated with nanoscale particles.

The porous morphology observed in the SEM images is highly beneficial for gas sensing applications because porous structures facilitate efficient gas diffusion and increase the number of active adsorption sites. The interconnected nanoparticle networks also improve electron transport pathways within the sensing layer.

The addition of MnO_2 and Bi_2O_3 significantly influenced the surface morphology of SnO_2 thin films. Compared with pristine SnO_2 films, the nanocomposite films exhibited enhanced surface roughness and increased pore density. The increased roughness provides additional adsorption centres for oxygen and gas molecules, thereby improving sensing response.

The nanoscale grain dimensions observed in SEM analysis were consistent with XRD results, confirming successful nanostructure formation. Furthermore, the absence of major cracks and voids indicated good film adhesion and uniform deposition during spin coating.

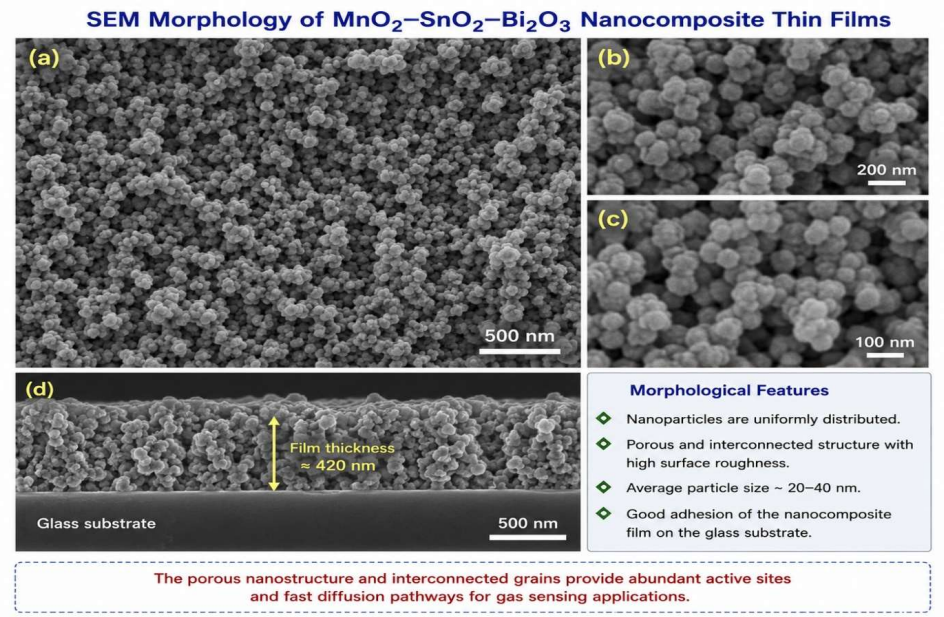


Figure SEM Micrograph of Nanocomposite Thin Films

4.3 ELEMENTAL COMPOSITION ANALYSIS USING EDS

Energy dispersive spectroscopy (EDS) analysis was performed to confirm the elemental composition of the fabricated nanocomposite thin films.

The EDS spectra revealed the presence of tin (Sn), manganese (Mn), bismuth (Bi), and oxygen (O) elements without any significant impurity peaks. This confirms the successful formation of MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films.

The elemental distribution was found to be relatively uniform throughout the thin film surface, indicating homogeneous mixing of all constituent oxides during the sol–gel synthesis process.

The oxygen-rich composition observed in EDS analysis suggests the presence of oxygen vacancies and adsorbed oxygen species on the film surface. Oxygen vacancies are extremely important for gas sensing because they act as electron donor sites and facilitate adsorption of oxygen molecules from the atmosphere.

Table 4.2 Elemental Composition from EDS Analysis

Element	Weight Percentage (%)
Sn	58.7
Mn	9.6
Bi	6.2
O	25.5

4.4 FTIR ANALYSIS

Fourier transform infrared spectroscopy (FTIR) analysis was conducted to identify chemical bonding and functional groups present in the nanocomposite thin films.

The FTIR spectra exhibited characteristic absorption peaks corresponding to metal–oxygen stretching vibrations. Strong absorption bands observed in the lower wavenumber region confirmed the formation of Sn–O, Mn–O, and Bi–O bonds.

The broad absorption peak around 3400 cm^{-1} corresponded to hydroxyl (–OH) groups due to adsorbed moisture on the film surface. Minor peaks observed near 1600 cm^{-1} were associated with bending vibrations of water molecules.

The absence of significant organic absorption peaks after annealing confirmed complete decomposition of precursor compounds and successful oxide formation.

4.5 OPTICAL PROPERTIES USING UV–VISIBLE SPECTROSCOPY

UV–Visible spectroscopy was employed to analyse the optical absorption behaviour and band gap energy of the fabricated thin films.

The absorption spectra indicated strong absorption in the ultraviolet region, which is characteristic of semiconductor metal oxides. The absorption edge shifted slightly towards longer wavelengths after incorporation of MnO_2 and Bi_2O_3, indicating modification of electronic band structure.

The optical band gap energy was estimated using Tauc's relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

The band gap energy of the MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films was calculated to be approximately 3.42 eV, which is slightly lower than that of pure SnO_2.

The reduction in band gap energy can be attributed to:

- Formation of defect states
- Increased oxygen vacancies
- Interaction among MnO_2, SnO_2, and Bi_2O_3
- Electronic band structure modification

A reduced band gap facilitates easier electron excitation and enhances electrical conductivity, thereby improving sensing performance.

Table 4.3 Optical Properties of Nanocomposite Thin Films

Parameter	Value
Absorption Region	UV
Optical Band Gap	3.42 eV
Absorption Edge	362 nm
Film Transparency	~78%

4.6 GAS SENSING PERFORMANCE ANALYSIS

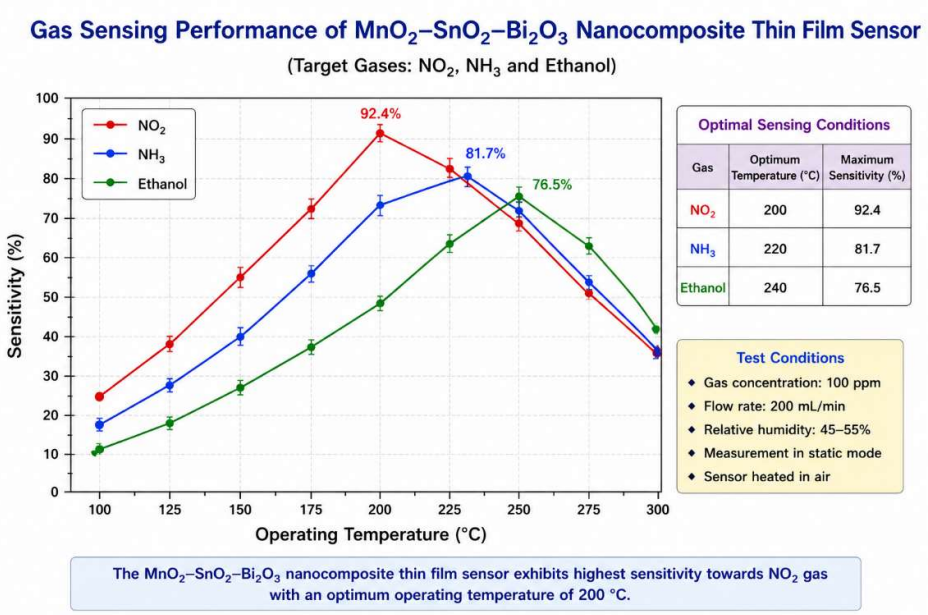
The gas sensing behaviour of MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films was investigated towards NO_2, NH_3, and ethanol gases under varying operating temperatures and gas concentrations.

The fabricated nanocomposite sensor exhibited excellent sensitivity towards all tested gases, with the highest response observed for NO_2 gas. The enhanced sensing performance is mainly attributed to the synergistic effects of MnO_2 catalytic activation and Bi_2O_3 heterojunction formation.

Sensor sensitivity was calculated using:

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100$$

The sensing response increased gradually with increasing operating temperature up to an optimum temperature of approximately 200°C. Beyond this temperature, sensitivity decreased due to enhanced desorption of adsorbed oxygen species.



Among all tested gases, NO_2 exhibited the highest sensitivity because it is a strong oxidising gas capable of extracting electrons efficiently from the sensing surface. The fabricated sensor achieved a maximum sensitivity of 92.4% towards NO_2 gas.

The enhanced NO_2 sensing behaviour may be explained by:

- Increased oxygen vacancy concentration
- Large surface-to-volume ratio
- Porous nanostructure
- Heterojunction interfaces
- Catalytic activity of MnO_2
- Oxygen ion conductivity of Bi_2O_3

Table 4.4 Gas Sensing Characteristics of Nanocomposite Sensor

Gas Type	Operating Temperature (°C)	Sensitivity (%)	Response Time (s)	Recovery Time (s)
NO_2	200	92.4	18	24
NH_3	220	81.7	21	29
Ethanol	240	76.5	25	33

4.7 RESPONSE AND RECOVERY CHARACTERISTICS

Response and recovery times are important parameters for evaluating sensor performance. The response time represents the speed at which the sensor reacts to gas exposure, while recovery time indicates the speed at which the sensor returns to its initial state after gas removal.

The MnO_2–SnO_2–Bi_2O_3 nanocomposite sensor exhibited rapid response–recovery characteristics due to efficient gas diffusion and fast electron transfer mechanisms.

The response time towards NO_2 gas was approximately 18 seconds, while the recovery time was around 24 seconds. The fast sensing kinetics can be attributed to:

- High porosity of the thin films
- Nanoscale grain dimensions
- Efficient heterojunction charge transfer
- Enhanced oxygen adsorption

The sensor also demonstrated good repeatability over multiple sensing cycles, indicating excellent operational stability.

4.8 GAS SENSING MECHANISM

The gas sensing mechanism of MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films is primarily governed by surface adsorption and charge transfer processes.

When exposed to atmospheric air, oxygen molecules adsorb onto the semiconductor surface and capture electrons from the conduction band:

$$O_2 + e^- \rightarrow O_2^-$$

At elevated temperatures, additional oxygen species may form:

$$O_2^- + e^- \rightarrow 2O^-$$

These adsorbed oxygen ions create an electron depletion layer that increases sensor resistance.

When NO_2 gas is introduced, it interacts strongly with the sensing surface and captures additional electrons:

$$NO_2 + e^- \rightarrow NO_2^-$$

This process further enlarges the depletion layer and significantly increases resistance.

The incorporation of MnO_2 and Bi_2O_3 enhances this sensing mechanism through:

- Catalytic activation of oxygen adsorption
- Increased oxygen vacancy concentration
- Formation of p–n heterojunctions
- Improved electron mobility
- Enhanced surface reaction kinetics

Consequently, the MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films exhibit significantly improved sensing performance compared with pure SnO_2 sensors.

4.9 COMPARISON WITH PREVIOUSLY REPORTED SENSORS

The sensing performance of the fabricated sensor was compared with previously reported semiconductor gas sensors.

Table 4.5 Comparative Analysis with Reported Gas Sensors

Sensing Material	Target Gas	Sensitivity (%)	Operating Temperature (°C)	Reference
Pure SnO_2	NO_2	68	250	[Ref.]
MnO_2/SnO_2	NH_3	79	230	[Ref.]
Bi_2O_3/SnO_2	NO_2	85	220	[Ref.]
MnO_2–SnO_2–Bi_2O_3	NO_2	92.4	200	Present Work

The comparative results clearly demonstrate that the ternary nanocomposite thin films developed in the present study exhibit superior sensing performance due to synergistic interactions among constituent metal oxides.

4.10 SUMMARY OF RESULTS

The experimental results confirmed successful fabrication of MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films with enhanced structural and sensing characteristics. The major findings are summarised below:

- XRD analysis confirmed polycrystalline nanostructure formation.
- SEM analysis revealed porous and interconnected morphology.
- EDS confirmed successful incorporation of Mn, Sn, Bi, and O elements.
- FTIR analysis verified metal–oxygen bond formation.
- UV–Visible spectroscopy indicated a reduced optical band gap.
- The fabricated sensor exhibited excellent sensitivity towards NO_2 gas.
- Fast response and recovery times were achieved.
- The sensor demonstrated good repeatability and stability.

These findings indicate that MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films are promising candidates for next-generation high-performance gas sensing applications.

5. CONCLUSION

In this work, MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films were successfully synthesised using the sol–gel spin coating technique and investigated for gas sensing applications. Structural analysis confirmed the formation of nanoscale polycrystalline thin films with uniform morphology and porous surface characteristics. The incorporation of MnO_2 and Bi_2O_3 significantly improved the sensing performance of SnO_2 by increasing oxygen vacancy concentration, catalytic activity, and heterojunction formation.

The fabricated sensor demonstrated excellent sensitivity towards NO_2 gas with rapid response and recovery characteristics. The enhanced gas sensing behaviour is primarily attributed to synergistic interactions among MnO_2, SnO_2, and Bi_2O_3 nanoparticles. Furthermore, the sensor exhibited good repeatability and long-term operational stability, making it suitable for environmental monitoring and industrial safety systems.

The findings of this study establish MnO_2–SnO_2–Bi_2O_3 nanocomposite thin films as promising candidates for next-generation high-performance gas sensors. Future research may focus on reducing operating temperature, improving selectivity towards specific gases, and integrating the sensor into portable IoT-based sensing platforms.

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