

Tailoring Oxygen Vacancies and Surface Morphology in Ni-Doped FeMnO₃ Thin Films for High-Performance Ammonia Sensing

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Tailoring Oxygen Vacancies and Surface Morphology in Ni-Doped FeMnO₃ Thin Films for High-Performance Ammonia Sensing

Abstract

Ammonia (NH₃) is a dangerous gas widely used in industrial and agricultural applications, and its rapid detection is essential for environmental monitoring and human safety. In this work, Pure and Ni-doped FeMnO₃ thin films were prepared by chemical spray pyrolysis and investigated for ambient-temperature ammonia gas sensing. X-ray diffraction analysis confirmed the formation of a crystalline cubic phase of FeMnO₃, and a slight shift in the diffraction peaks indicated the successful incorporation of Ni ions into the lattice. Surface morphology analysis revealed that Ni doping significantly modified the microstructure and increased surface roughness, thereby enhancing the number of active sites for gas adsorption. Among the fabricated samples, the 3 wt.% Ni-doped FeMnO₃ thin film (NFM2) exhibited the best ammonia selectivity of 67% at 100 ppm NH₃ at room temperature. The sensor also demonstrated rapid response and recovery times of 136 s and 94 s, respectively. These improvements are attributed to the synergistic effects of Ni- induced defect engineering, increased oxygen vacancy concentration, enhanced surface roughness, and improved charge transport. Furthermore, the fabricated sensor exhibited good humidity tolerance and good operational stability over seven weeks, demonstrating its reliability under ambient conditions. The developed sensor operates at room temperature without external heating, making it suitable for low-power sensing applications.

Keywords

Ammonia sensing, Spray pyrolysis, Nickel-doped FeMnO₃, Thin film, Resistive type.

1. Introduction

The detection and monitoring of toxic and hazardous gases have become increasingly important due to rapid industrialisation and environmental pollution.[1,2] . Ammonia (NH_3), a widely used industrial gas, plays a significant role in fertiliser manufacturing, agriculture, refrigeration systems, and the chemical industry. However, prolonged exposure to ammonia can seriously irritate the skin, eyes, and breathing system, endangering both human health and the environment [3].

Metal oxide semiconductor (MOS) gas sensors have also become promising due to their high sensitivity, simple device structure, cost-effectiveness, and ease of fabrication [4]. Nanostructured metal oxide films have been extensively studied for gas sensing, including ZnO [5], SnO_2 [6], CuO [7], Fe_2O_3 [8], and MnO_2 [9]. The sensing mechanism of MOS sensors is largely based on the adsorption and desorption of oxygen species at the sensing material's surface, resulting in a large change in electrical resistance when interacting with target gas molecules. Ammonia sensing at room temperature is highly desirable because external heating is not required, reducing power consumption and enabling its use in low-power sensing devices [10].

Mixed transition-metal oxides have attracted significant attention over the past few years due to their distinctive structural properties, high electrical conductivity, and catalytic activity. FeMnO_3 has become a promising sensing material due to its multiple oxidation states, strong redox properties, and efficient electron transport [11,12]. Moreover, doping with transition metals is believed to be an efficient way to improve the sensing behaviour of metal oxide materials by altering the electronic structure, increasing the concentration of oxygen vacancies, and enhancing surface reactivity [13,14]. Nickel (Ni) doping can introduce additional defect states and catalytically active sites into the FeMnO_3 lattice, thereby facilitating gas adsorption and charge transfer.

Although several transition-metal-doped metal oxide semiconductors have been reported for room-temperature ammonia sensing, direct correlations among Ni-induced defect engineering, oxygen-vacancy generation, carrier transport, and sensing enhancement remain limited. Comprehensive studies that combine structural, electrical, and surface chemical characterisations to elucidate the room-temperature sensing mechanism of Ni-doped FeMnO_3

thin films remain scarce. Therefore, further investigation is required to understand the relationship between defect formation and sensing performance.

In addition to the composition of the materials, the method used to fabricate thin films is also significant in defining their structural and sensing characteristics. Spray pyrolysis is a simple, low-cost, and scalable method for producing uniform layers of metal oxides with precise composition and morphology [15,16]. The technique provides very good control over film thickness, microstructure, and dopant concentration, which makes it applicable to gas sensing.

The present work focuses on room-temperature sensing to eliminate the need for external heating, thereby reducing power consumption and improving the feasibility of portable gas-sensing devices. In this study, Ni-doped FeMnO₃ thin films were fabricated by spray pyrolysis and systematically studied for ammonia gas sensing at room temperature. Ni doping effects on the structural, morphological, optical and electrical properties of FeMnO₃ thin films were well studied. Additionally, sensitivity, response-recovery properties, selectivity of the prepared films, and their stability in humidity were determined for ammonia gas sensing. The Ni doping dramatically improves the performance of FeMnO₃ thin films as sensing elements, suggesting the potential for efficient room-temperature ammonia gas sensing. Furthermore, the sensing enhancement mechanism is systematically correlated with the structural, morphological, electrical, and surface chemical properties of the films using XRD, FESEM, AFM, Hall-effect measurements, and XPS. To the best of our knowledge, this is one of the few reports investigating Ni-induced oxygen vacancy engineering in spray-pyrolysed FeMnO₃ thin films for room-temperature ammonia sensing.

2. Experimental Methods

2.1 Materials Synthesis

The precursor materials used in this study were Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), Manganese (II) acetate tetrahydrate (Mn(C₂H₃O₂)₂·4H₂O), and Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O). Ni-doped FeMnO₃ thin films containing 0, 1, 3 and 5 wt.% Ni were deposited on glass substrates using the chemical spray pyrolysis technique. Initially, 0.05 M aqueous solutions of iron nitrate, manganese acetate, and nickel nitrate were prepared separately by dissolving the required amounts of each precursor in 30 mL of double-distilled

water, as shown in the Figure. 1(a). The precursor solutions were continuously stirred for 20 min before deposition. The solution was then sprayed onto the cleaned substrates at 220°C. The distance between the nozzle and the substrate was kept constant at 30 cm. The nozzle was kept at a 45° angle. The spray rate of the precursor solution was 3 mL/min. The spray lasted over 5 seconds. Approximately 120 spray cycles were used to deposit the entire precursor solution. The schematic diagram for spray pyrolysis is depicted in Figure. 2(b). Homogeneous brown thin films are presented in the Figure. 1(c). The prepared thin films were annealed at 400°C for 1 h in air. The films have been labelled NFM0, NFM1, NFM2, and NFM3, depending on their dopant concentration (0, 1, 3, and 5 wt.%).

2.2 Thin Film Characterization

The X-ray diffraction analysis was carried out on the Malvern Empryean (Malvern PANalytical, Netherlands), where the sample was subjected to a temperature scan from 20°C up to 80°C as well as employing Cu K α 1 X-ray source ($\lambda = 1.5405 \text{ \AA}$) for Cu K α 1 radiation. Furthermore, surface morphology studies were performed utilising a Field Emission Scanning Electron Microscope (CARL ZEISS-SIGMA 300) along with Energy-Dispersive X-ray Spectroscopy. Surface topography was studied using the (OXFORD MFP 3d Origin) for Atomic Force Microscopy. The elemental composition and chemical states of the thin film were determined using an X-ray photoelectron spectrometer (K-Alpha -KAN 9954133, Thermo Scientific).

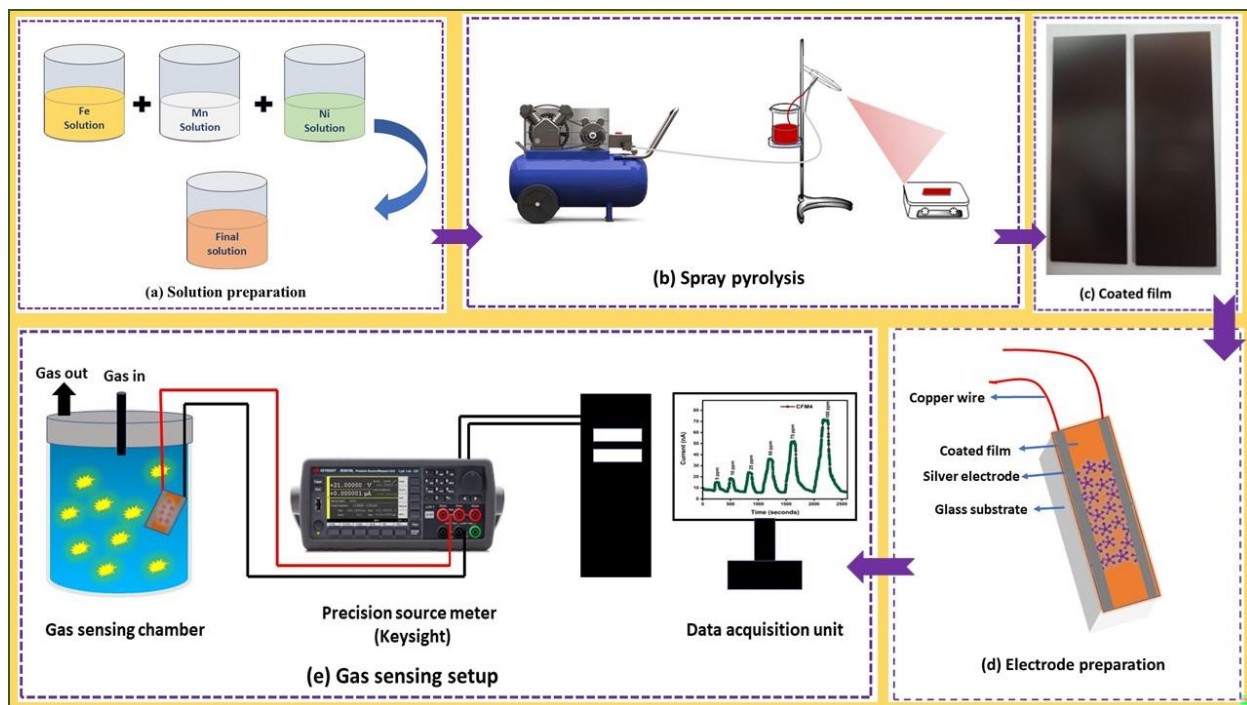


Figure 1. (a) Preparation of the solution process, (b) diagram of a spray pyrolysis unit, (c) coated NFM thin film, (d) electrode preparation, and (e) Gas sensing setup.

2.3 Gas Sensing Measurements

The sensors were fabricated on Nickel doped Iron Manganese Oxide thin films and measured in a gas-sensing setup designed for volatile organic compounds. Silver conducting paste and high-conductivity copper wire were used at the contact points. At room temperature, we use a homemade setup for detecting target gases. Initially, the Nickel-doped Iron Manganese Oxide thin film sensor was placed to ensure it reached a stable reading. To determine gas responses, baseline resistance or current is necessary. A Nickel-doped Iron Manganese Oxide thin film sensor is point-contacted, and the Keysight source measure unit (B2900) is linked to it and enclosed in the gas chamber unit. To stabilise the baseline resistance, the sensor was initially kept in ambient air until a stable current was introduced to the target gas. The number of target gases was then determined, and the liquids were injected into the chamber. Due to their interaction with the sensor film, the baseline current is raised. The sensor response was analysed as the ratio between the baseline current measurements in gas and air. The equation used to calculate the sensor response (Eq. 1) [17,18]:

$$S = I_g/I_a \quad (1)$$

The sensor response and recovery times were determined as the times required to achieve 90% of the gas response during adsorption and desorption, respectively. Additionally, the behavior of the thin-film sensors was observed under different humidity conditions, and their performance was evaluated. Since the objective of the present work was to develop a low-power ammonia sensor operating under ambient conditions, all sensing measurements were intentionally performed at room temperature without external heating. For the targeted gas concentration, the static liquid-gas sensing method was used. The equation used to calculate the gas concentration (C) (Eq. 2) [19,20]:

$$C_{ppm} = \frac{\rho V_l R T \times 10^6}{P_b M_w V_b} \quad (2)$$

In this expression, ρ represents the density of the liquid (kg/m^3), V_l denotes the evaporated liquid volume (m^3), T is the absolute temperature (K), R corresponds to the ideal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), P_b indicated the chamber pressure (Pa), M_w refers to the molecular weight of the target gas (kg/mol^{-1}), and V_b is the total volume of the gas chamber (m^3). Analytical grade chemicals were used throughout the experiments. Ammonia solution ($\geq 25\%$ NH_3 in H_2O , density = 0.91 g/mL), ethanol (99.9%, density = 0.79 g/mL), 2-propanol ($\geq 99.7\%$, density = 0.77 g/mL), 1-butanol ($\geq 98\%$, density = 0.81 g/mL), and benzene ($\geq 99\%$, density = 0.88 g/mL), Acetone ($\geq 99\%$, density = 0.79 g/mL), were purchased from commercial suppliers.

3. Result and discussion

3.1 Structural analysis

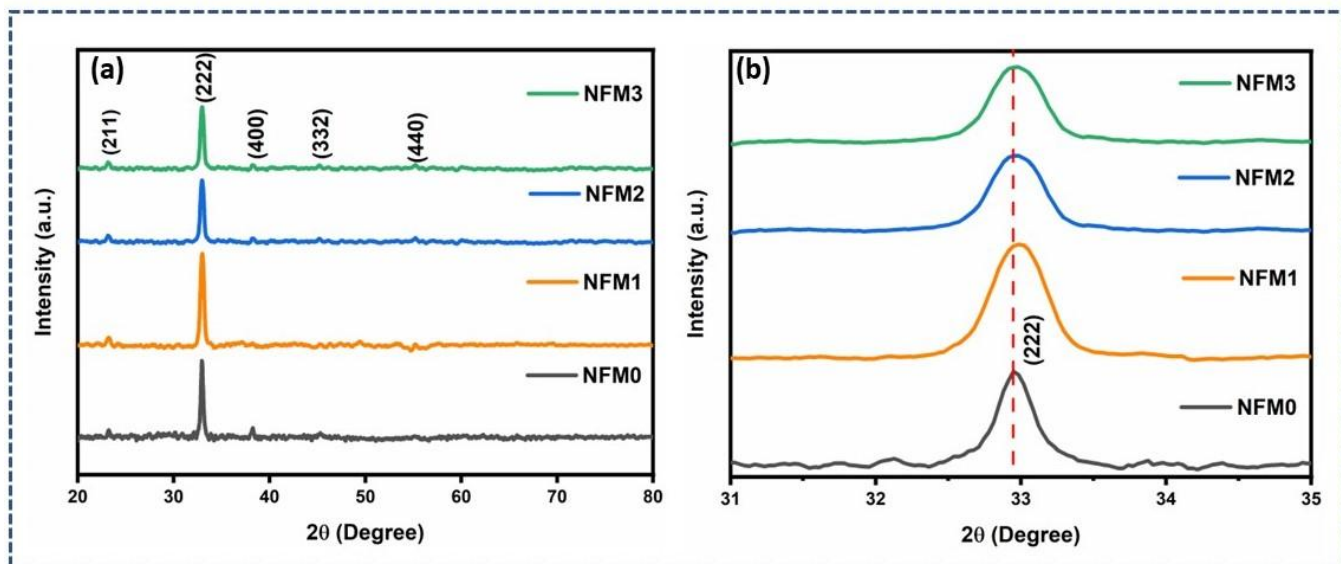


Figure. 2. (a) XRD pattern of Pure and Ni-doped FeMnO_3 films, (b) A magnified view of the XRD pattern - 31 to 35°.

Figure. 2(a) presents the XRD pattern of pure and Ni-doped FeMnO_3 thin films. The diffraction peaks were assigned to the (211), (222), (400), (332), and (440) planes, which correspond well to the standard Reference code 01-075-1573, indicating the cubic perovskite structure [15]. The (222) diffraction peak exhibited the highest intensity, and the maximum intensity of this plane drops as the Ni dopant concentration rises. This reduction may be attributed to the incorporation of Ni ions into the FeMnO_3 lattice, inducing lattice distortions and defect states. Figure. 2(b) reveals a slight shift in the higher 2θ values with increasing Ni content. According to Bragg's law, variations in the distance between atomic planes directly influence the position of diffraction peaks. The incorporation of Ni ions in the FeMnO_3 lattice in place of Mn results in lattice contraction, which can be attributed to the smaller ionic radius of Ni (0.56 Å) compared to Mn (0.64 Å). As a result, the diffraction peaks shift slightly towards higher values. This peak shift indicates a reduction in both the lattice parameter and unit cell volume with increasing Ni concentration, confirming the successful substitution of Ni ions into the FeMnO_3 lattice. The lattice contraction induced by Ni substitution generates localised lattice distortions and defect states, thereby facilitating the formation of oxygen vacancies. These defects promote efficient electron transport and provide additional active adsorption sites for oxygen species,

thereby enhancing room-temperature ammonia sensing performance. Cell volume showed a similar pattern, declining from 829.3 Å³ to 814.2 Å³. The average crystallite sizes for NFM0, NFM1, NFM2, and NFM3 thin films were determined using the Scherrer formula to be 15.08 nm, 18.49 nm, 19.82 nm, and 17.05 nm, respectively. The Debye-Scherrer equation (Eq. 3) was used to determine the crystallite size (D) [16]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where λ is the X-ray wavelength (Cu K α 1, 1.5405 Å), θ is the Bragg angle, β is the full width at half maximum (FWHM), and k is the form factor (assumed to be 0.94). The following equation (Eq. 4) was used to compute the lattice strain (ϵ), which represents the degree of lattice distortion [18]:

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

Where ϵ represents microstrain in radians, β is the FWHM, and θ is the Bragg angle. The slight shift of the (222) peak toward higher 2θ values with Ni doping indicates a decrease in interplanar spacing and a contraction of the lattice. The recalculated lattice parameters in Table 1 show a gradual decrease in the lattice constant and unit cell volume as the Ni content increases, confirming lattice contraction.

Table 1

Lattice constant, microstrain, dislocation density, crystallite size and cell volume of pure and Ni-doped FeMnO₃ films.

Sample code	Lattice constant (Å) a=b=c	Microstrain (10 ⁻³)	Crystallite size (nm)	Cell volume (V) Å ³	Dislocation density x10 ⁻³ (nm ⁻²)
NFM0	9.403	1.5	15.08	829.3	3.841
NFM1	9.386	1.7	18.49	824.6	2.928
NFM2	9.364	1.9	19.82	820.1	2.543
NFM3	9.341	1.7	17.05	814.2	2.654

The gradual decrease in lattice constant and unit cell volume further confirms the successful incorporation of Ni ions into the FeMnO_3 lattice. The induced lattice distortion is expected to increase defect density and oxygen vacancy concentration, both of which are beneficial for improving gas-sensing characteristics.

3.2 Field emission scanning electron microscope analysis

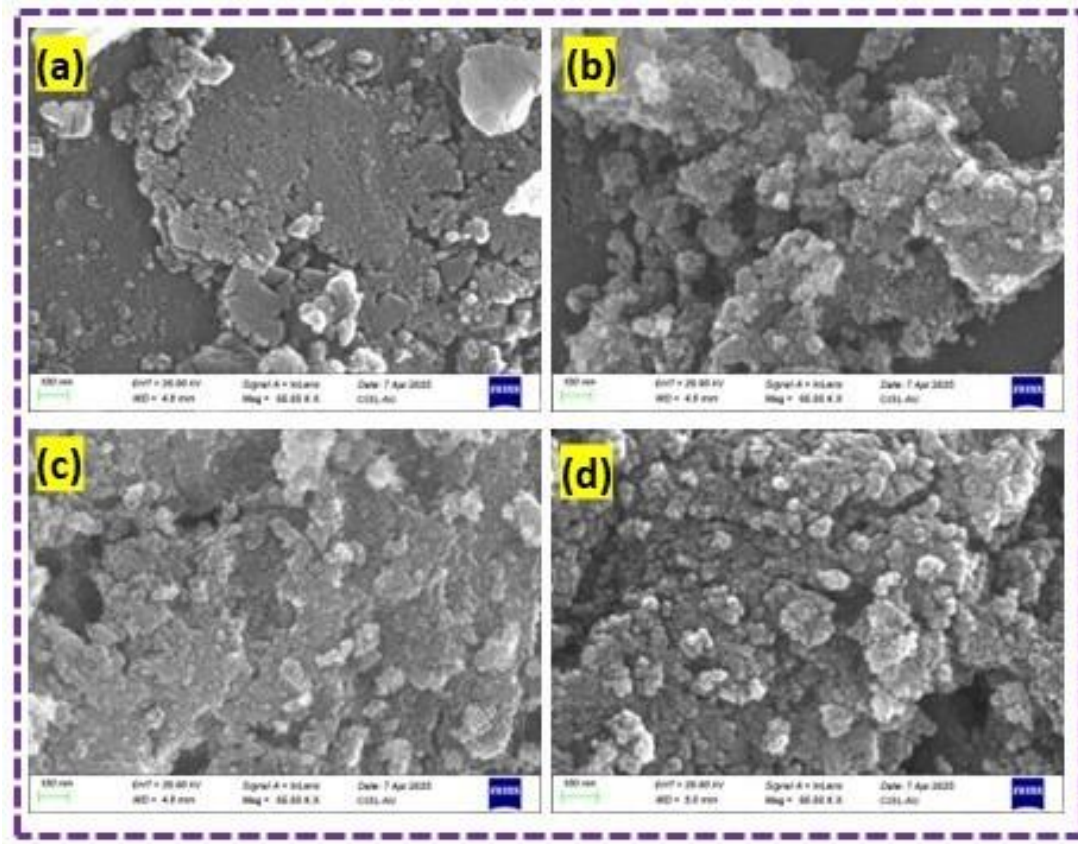


Figure (3). FESEM image of (a) NFM0 film, (b) NFM1 film, (c) NFM2 film, and (d) NFM3 film.

Field-emission scanning electron microscopy (FESEM) coupled with energy-dispersive X-ray spectroscopy (EDS) was employed to investigate the effect of Ni doping on the surface morphology and elemental composition of FeMnO_3 thin films. The FESEM micrographs shown in Figure 3(a–d) reveal a gradual evolution in surface morphology with increasing Ni concentration. The NFM0 sample exhibits irregularly distributed, agglomerated grains with relatively poor interparticle connectivity, thereby limiting the effective surface area available for

gas adsorption. Upon the introduction of NFM1, the grains become more uniformly distributed with improved grain connectivity, indicating that Ni incorporation influences the nucleation and growth behaviour of the FeMnO_3 thin films. Among all the prepared samples, the NFM2 film exhibits a homogeneous porous morphology with uniformly distributed interconnected grains. This optimised microstructure provides a larger active surface area and facilitates efficient diffusion of NH_3 molecules throughout the sensing layer. The increased number of exposed grain boundaries enhances the adsorption of oxygen species and promotes charge transfer during the sensing process, resulting in the highest ammonia sensing response [5–7]. In contrast, the NFM3 film exhibits a relatively compact morphology while retaining its porous nature. The increased compactness may slightly reduce the accessibility of active adsorption sites, leading to a marginal decrease in sensing response compared with the NFM2 film. These observations suggest that 3 wt.% Ni provides the optimum surface morphology for room-temperature ammonia sensing.

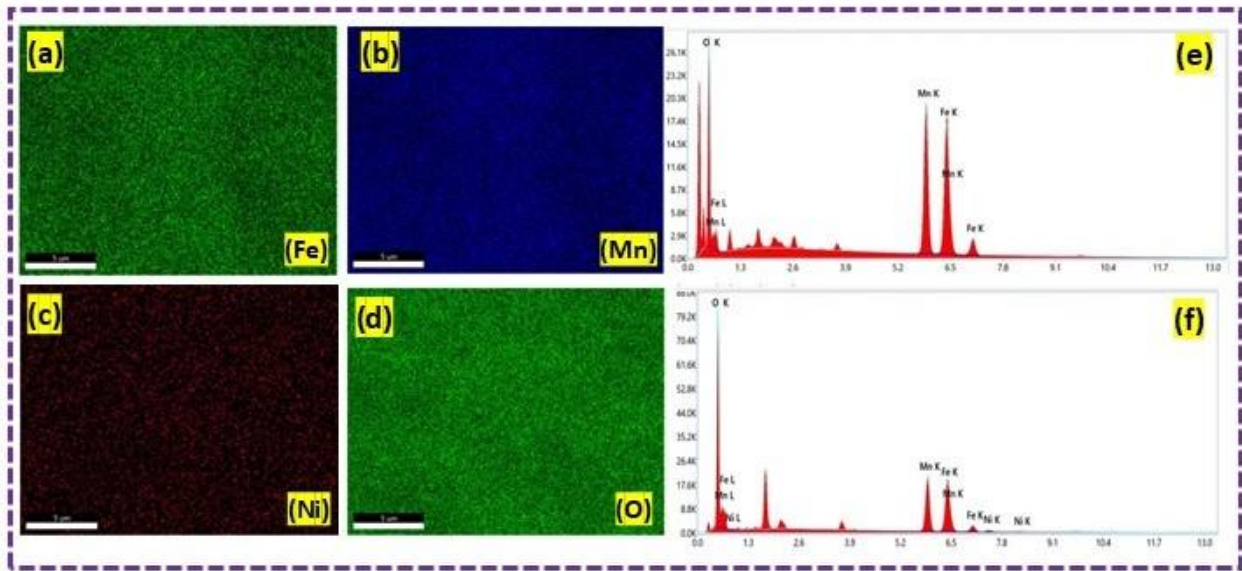


Figure. (4). Element mapping images of (a) Fe, (b) Mn, (c) Ni, (d) O and EDS spectrum of (e) undoped, (f) 3 wt.% Ni-doped FeMnO_3 films.

The EDS spectra of Figure 4 (a-d) confirmed the existence of primary elements of Fe, Mn, Ni and O, which confirmed the presence of FeMnO_3 . A weak Ni signal was detected in the doped film, confirming the presence of Ni in the FeMnO_3 matrix. Figure 4 (e, f) demonstrates the uniform distribution of Fe, Mn and O with localised Ni signals in element mapping images. The

homogeneous elemental distribution confirms the successful incorporation of Ni into the FeMnO_3 matrix, with no observable elemental segregation. The uniform elemental distribution is expected to contribute to stable electrical characteristics and reproducible gas-sensing behaviors [8].

3.3 Transmission electron microscope (TEM)

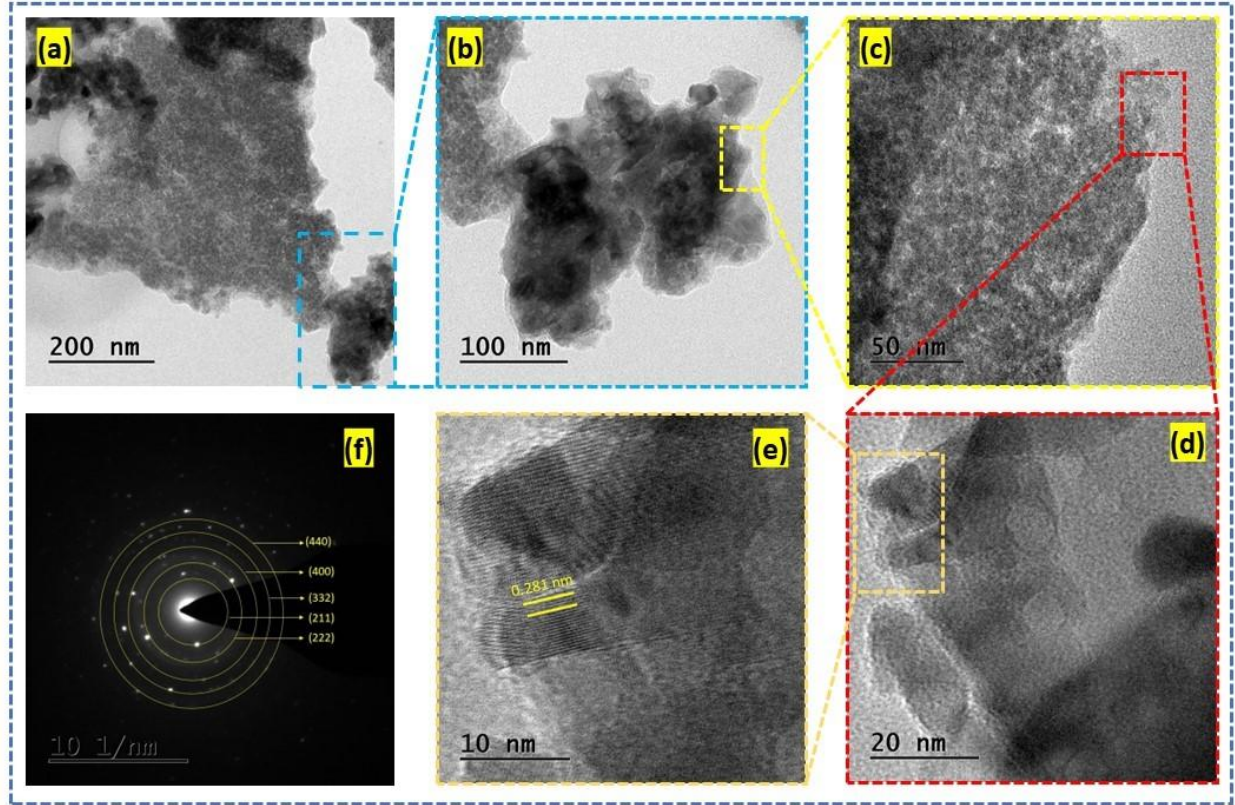


Figure. (6) (a-e) HR-TEM images of NFM0 film, and (f) NFM0 film SAED pattern

A comprehensive TEM and HR-TEM investigation of the NFM0 thin film is shown in Figure 6 to emphasise its nanoscale structural and morphological features. The film is made up of aggregated nanoparticles that form a highly porous, nanograined network, as demonstrated by the TEM images in Figure 6(a–b). With its increased surface area and improved diffusion channels, this porous shape is advantageous for applications such as gas detection and catalysis. The porous nanostructure provides abundant surface-active sites for oxygen adsorption and facilitates the rapid diffusion of ammonia molecules throughout the sensing layer. Such structural characteristics are beneficial for enhancing room-temperature sensing performance.

The homogeneity and even distribution of nanograins throughout the film are further supported by Figure 6(c–d). According to the standard JCPDS card no. 01-075-1573 [21]. The high-resolution TEM image 6 (e) shows well-resolved lattice fringes with an interplanar spacing of 0.281 nm, matching the (222) plane of cubic FeMnO_3 . This lattice spacing supports the high crystallinity and phase purity of the developed material. Furthermore, a polycrystalline structure is indicated by a series of bright, sharp concentric rings in the selected area electron diffraction (SAED) pattern shown in Figure 7(f). The cubic perovskite FeMnO_3 structure's (211), (222), (400), (322), and (440) planes were assigned to the rings. Using ImageJ software, the corresponding d-spacings were determined to be 3.734 Å, 2.735 Å, 2.563 Å, 2.245 Å, and 1.568 Å, respectively. The presence of a well-crystallised perovskite phase and the random orientation of nanocrystallites are further supported by the transparent diffraction rings. The observed polycrystalline nature is consistent with the XRD analysis, confirming the formation of highly crystalline FeMnO_3 thin films after post-deposition annealing.

3.4 Optical Characterization

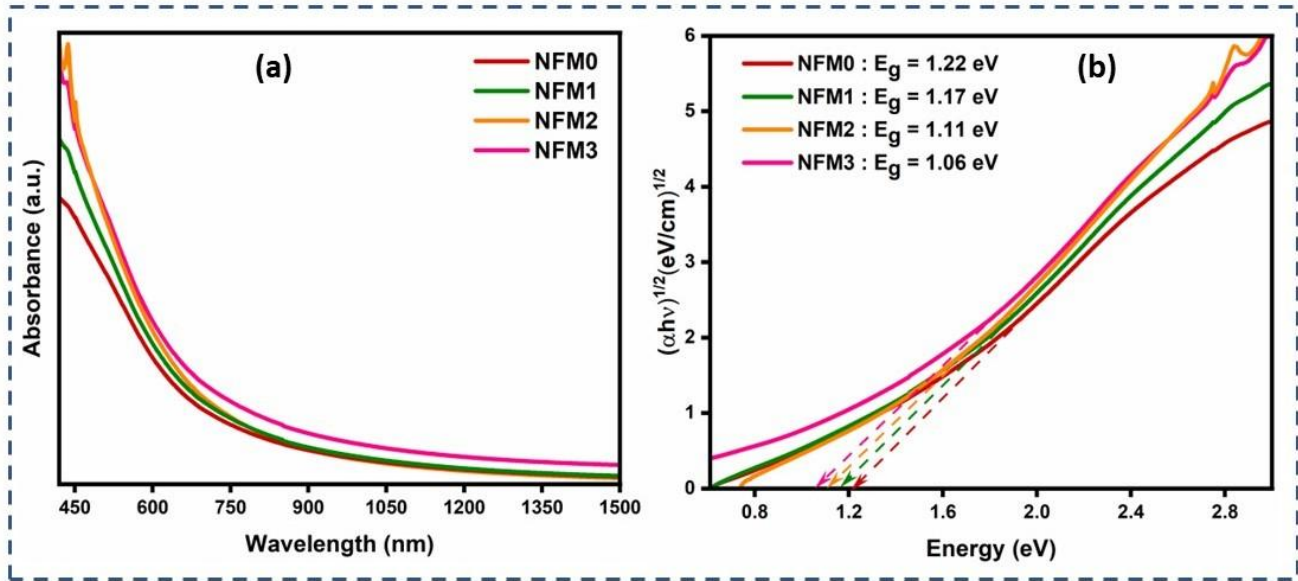


Figure. (7). (a) Absorption spectra, and (b) calculated bandgap energy of Pure and different Ni concentration doped FeMnO_3 thin films.

Optical properties of Pure and Nickel-doped FeMnO₃ thin films have been characterised using the technique of UV–Visible spectroscopy. The absorbance spectrum of the Nickel-doped FeMnO₃ films (NFM0 to NFM3) is shown in Figure 7(a). All the samples used showed prominent absorption in the UV–Visible range. To estimate the optical band gap energy (E_g), the absorption data were fitted by Tauc plots, as shown in Fig. 7(b). Electronic transitions in FeMnO₃-based materials are of an indirect nature, Tauc plot Eq. (5) [22] below.

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (5)$$

where A represents a material constant, $h\nu$ denotes the photon energy, and α denotes the absorption coefficient. Extrapolation of the linear part of the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots gave the band gap energies of the respective samples. The band gap values for NFM0, NFM1, NFM2, and NFM3 were 1.22 eV, 1.17 eV, 1.11 eV, and 1.06 eV, respectively. Systematic band-gap reduction with increasing nickel doping resulted in a redshift of the absorption edge. In this study, the reduction in band gap energy due to Nickel doping is attributed to defect generation, oxygen vacancies, increased lattice strain, and changes in carrier density and crystallite size. Ni incorporation introduces localised defect states and oxygen-vacancy-related energy levels within the band gap, resulting in absorption-edge tailing and a gradual reduction in the optical band gap energy. These defect-induced intermediate energy levels facilitate electronic transitions and enhance carrier excitation, thereby improving charge transport during room-temperature gas sensing.

3.5 Atomic force microscopy analysis

The grain morphology and surface roughness of the films were examined using atomic force microscopy (AFM). The topographic images were recorded in contact mode over an area of $5 \times 5 \mu\text{m}^2$ to assess the growth quality, grain distribution, and surface roughness of the NFM thin films, as illustrated in the Figure. 8. All samples exhibited a rough, dense, and crack-free surface. The calculated root-mean-square roughness (R_a) and average surface roughness (S_a) values for the deposited thin films were approximately 267, 283, 294, and 272 nm, and 234, 247, 264, and 239 nm, for the samples NFM0, NFM1, NFM2, and NFM3, respectively. Among these, NFM2 exhibited the highest surface roughness, attributed to the optimal Ni doping level of 3 wt%. Higher surface roughness increases the effective surface area and enhances the number of

gas adsorption sites, thereby improving the interaction between ammonia molecules and the sensing layer. Among all the prepared samples, the NFM2 thin film exhibited the highest sensing response owing to its optimized surface roughness and well-developed porous morphology. The increased surface roughness enhances the effective surface area available for oxygen adsorption, leading to a higher concentration of chemisorbed oxygen species. Consequently, the probability of interaction between NH_3 molecules and the sensing surface increases significantly, thereby enhancing the sensing response. This enhanced behaviour can be attributed to its relatively high surface roughness, which provides more active sites for gas-molecule adsorption. Further, the film has a well-optimised microstructure, characterised by appropriate grain sizes and uniformly distributed porosity, which promotes efficient gas diffusion in the sensing film. These structural features enhance gas species interactions with reactive sites, leading to a larger response magnitude and improved sensing dynamics. The combined effects of high surface roughness, high oxygen vacancy concentration, a well-developed porous structure, and enhanced charge conduction result in excellent sensing performance in the NFM2 film. The active surface area increases with greater irregularity, and adsorption efficiency improves, which is an advantage in sensing applications. [23–25]. These observations confirm that an optimum Ni concentration effectively tailors the surface morphology of FeMnO_3 thin films, thereby improving their suitability for room-temperature ammonia sensing applications [26,27].

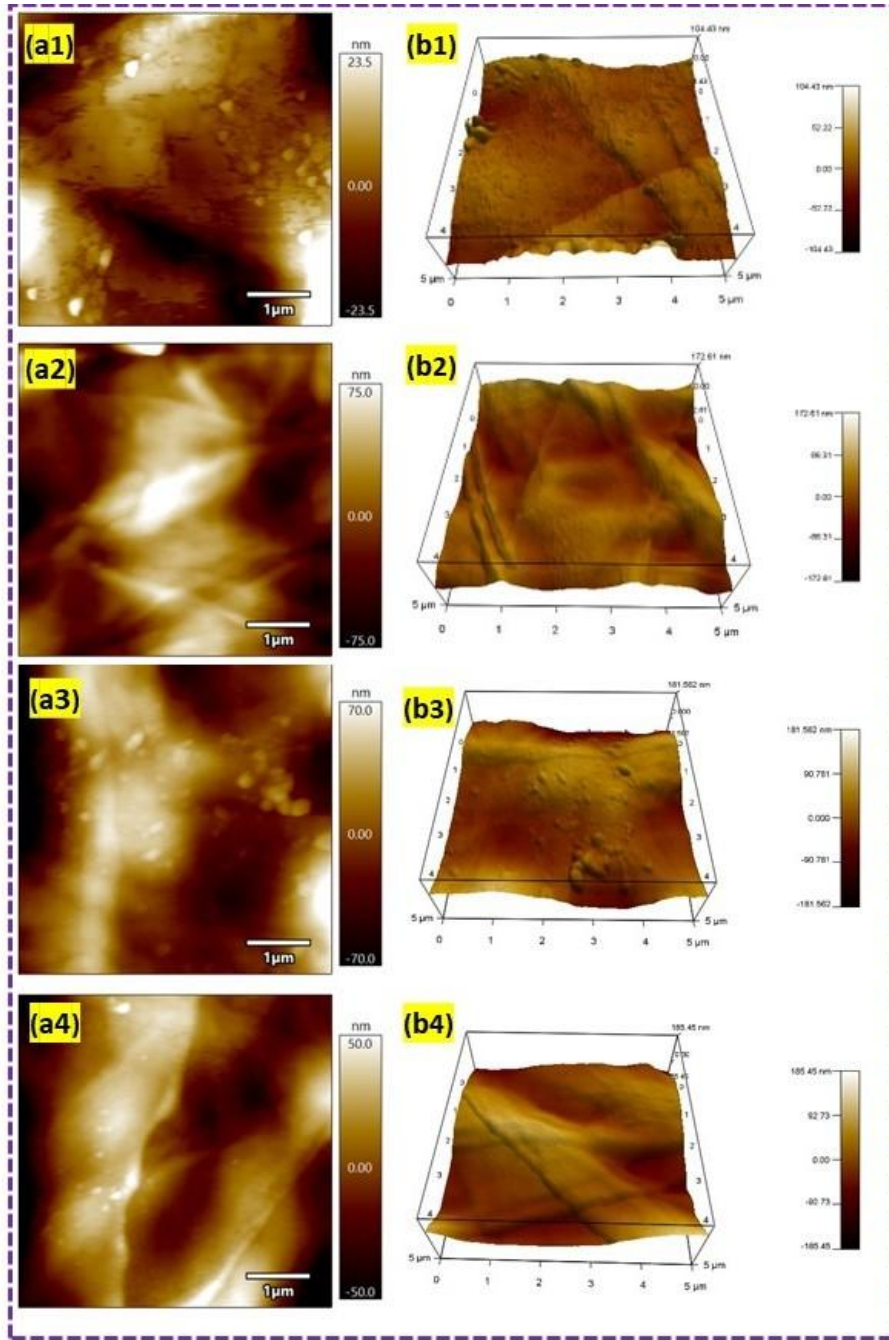


Figure. (8). Two- and three-dimensional AFM images of (a1, b1) NFM0, (a2, b2) NFM1, (a3, b3) NFM2, and (a4, b4) NFM3 films.

3.6 Hall-Effect Measurement

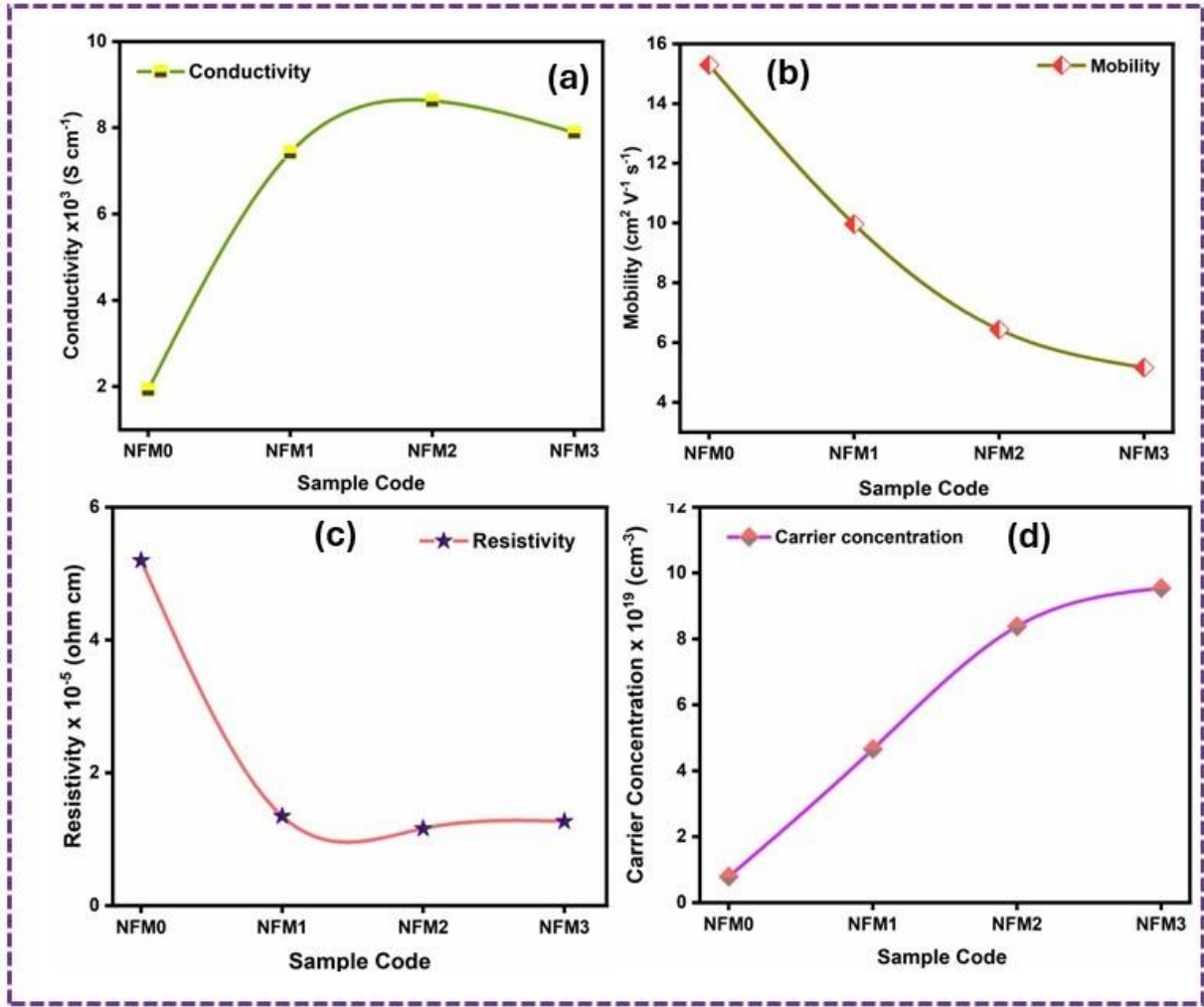


Figure. (9). Hall measurements (a) conductivity, (b) mobility, (c) resistivity & (d) carrier concentration of pure and Ni-doped FeMnO₃ thin films.

Hall-effect measurements were performed at ambient temperature to evaluate the electrical characteristics of Nickel-doped FeMnO₃ thin films, and the results are presented in the figure. 9(a–d). NFM0, NFM1, NFM2, and NFM3 samples exhibited n-type semiconductor behaviour, as evidenced by the negative carrier concentration. The carrier concentration of the undoped NFM0 sample was $7.86 \times 10^{18} \text{ cm}^{-3}$, which increased with increasing Ni content, reaching $8.38 \times 10^{19} \text{ cm}^{-3}$ for NFM3. The increase in carrier concentration with Ni incorporation is attributed to defect-assisted charge carrier generation and the formation of oxygen vacancies, which facilitate electron transport within the FeMnO₃ lattice.[28]. Although carrier mobility

gradually decreases due to increased impurity scattering, the higher carrier concentration, together with improved grain connectivity, results in enhanced electrical conductivity. The enhanced electrical conductivity facilitates rapid electron transfer between chemisorbed oxygen species and ammonia molecules, thereby contributing to the superior sensing performance of the optimised NFM2 thin film. Nickel incorporation alters the electronic structure and promotes the formation of oxygen vacancies, thereby facilitating electron transport in the film. As a result, the total resistivity does not increase even though the carrier concentration increases. Electrical resistivity decreased significantly upon Ni doping. While the undoped film exhibited a resistivity of $5.196 \times 10^{-4} \Omega \text{ cm}$, the doped samples showed significantly lower resistivities of $1.160 \times 10^{-4} \Omega \text{ cm}$ to $1.347 \times 10^{-4} \Omega \text{ cm}$. This behaviour suggests enhanced electrical conductivity in the doped films, likely due to improved film crystallinity, increased grain connectivity, or modified electronic structure. However, a slight increase in resistivity at higher doping levels in NFM3 may result from increased carrier scattering or the onset of defect-induced carrier trapping. A reduction in carrier mobility was observed with increasing Ni concentration, decreasing from $1.529 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in NFM0 to $5.163 \times 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in NFM3. The decrease in carrier mobility is mainly attributed to increased impurity scattering and defect formation induced by Ni incorporation in the FeMnO_3 lattice. Although reduced, the combined impact of moderate carrier concentration, low resistivity, and tunable mobility renders these Ni-doped FeMnO_3 thin films promising candidates for resistive-type gas-sensing applications, in which electron transport and surface activity are vital to sensor performance.

Table 2. Electrical Characterization of Spray Coated Ni-Doped FeMnO_3 thin Films.

Sample code	Carrier Concentration (cm^{-3})	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Resistivity ($\Omega \text{ cm}$)	Conductivity
NFM0	7.86×10^{18}	1.529×10^3	5.196×10^{-4}	1.924×10^3
NFM1	4.66×10^{19}	9.963×10^2	1.347×10^{-4}	7.424×10^3
NFM2	8.38×10^{19}	6.433×10^2	1.160×10^{-4}	8.621×10^3
NFM3	9.54×10^{19}	5.163×10^2	1.268×10^{-4}	7.886×10^3

3.7 X-ray Photoelectron Spectroscopy

The surface elemental composition and oxidation states of the FeMnO₃ sensing film were analysed using X-ray photoelectron spectroscopy (XPS). The broad scan spectrum Figure 10. (a) confirms the presence of Fe, Mn, Ni, and O elements, with binding energy peaks corresponding to Fe 2p, Mn 2p, Ni 2p and O 1s. The minor C 1s peak located at approximately 285 eV originates from adventitious carbon and was used for binding-energy calibration. Figure 10. (b) shows the Fe 2p spectrum with two distant peaks centred around 710.5 eV and 723.9 eV corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} with a satellite feature, confirming the presence of the Fe³⁺ state [29,30]. Figure 10 (c) shows the high-resolution Mn 2p spectrum, which displays two well-separated peaks at 641.4 eV and 653.2 eV corresponding to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively, indicating the presence of the Mn³⁺ oxidation state [31,32], which enhances redox activity and is beneficial for gas sensing. Figure 10 (d) shows that the high-resolution Ni 2p spectrum confirms the successful incorporation of Ni species into the FeMnO₃ lattice. Although the Ni concentration is relatively low, the observed Ni 2p peaks indicate the presence of oxidised Ni species contributing to defect formation within the host lattice, the presence of Ni³⁺ species with a peak around 856 eV [33,34]. Figure 10 (e) shows that the O1s spectrum is deconvoluted into three components: The binding energy peak at 529.6 eV is related to lattice oxygen (O₁), whereas the peak at 530.7 eV indicates oxygen vacancies with lower coordination (O₂), and the peak at 532.4 eV arises from oxygen species adsorbed on the surface (O₃) [35]. The relatively high concentration of oxygen-vacancy-related oxygen species (O₂) confirms that Ni incorporation promotes defect generation within the FeMnO₃ lattice. These oxygen vacancies serve as active adsorption centres for oxygen molecules, thereby facilitating electron exchange during ammonia sensing.[36–38]. The XPS results strongly support the proposed sensing mechanism by confirming the coexistence of lattice oxygen, oxygen-vacancy-related species, and chemisorbed oxygen. These surface-active species play a decisive role in improving the room-temperature sensing characteristics of the Ni-doped FeMnO₃ thin films.

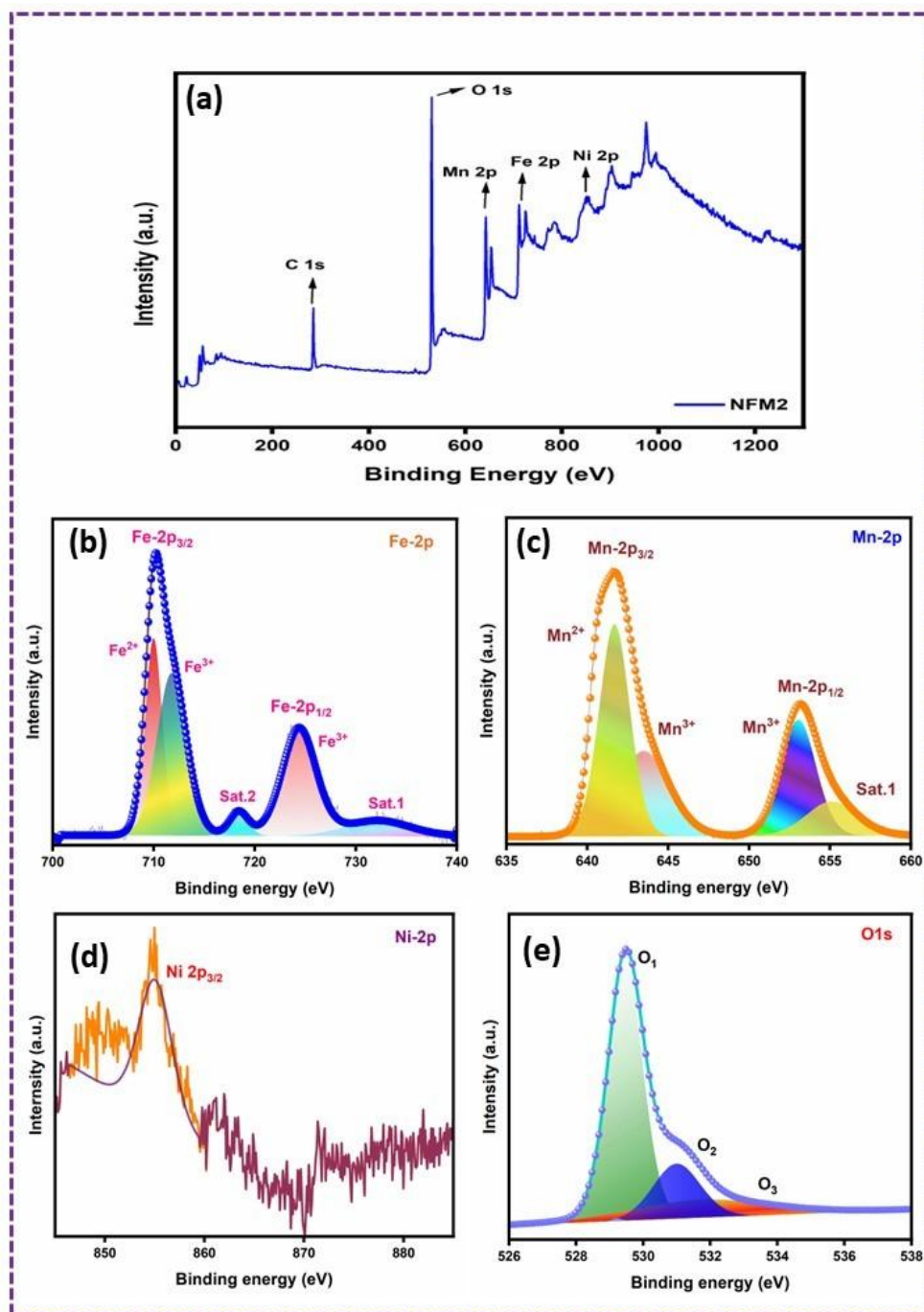


Figure 10. (a) Survey spectrum, (b) narrow scan of Fe, (c) narrow scan of Mn, (d) narrow scan of Ni, and (e) narrow scan of O for the NFM2 thin film.

3.8 Gas sensing measurement

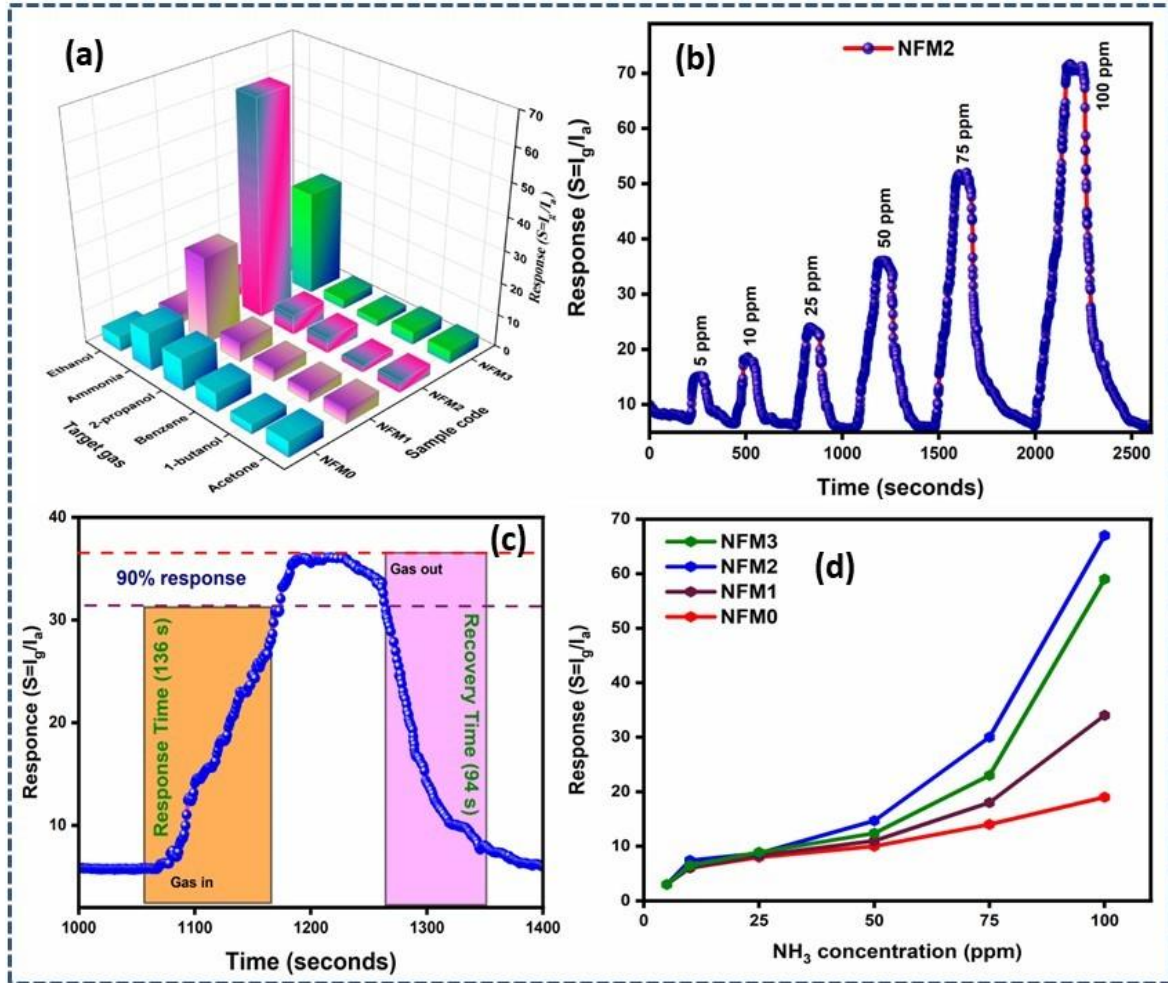


Figure. 11. (a) 100 ppm concentration of various gases at room temperature tested with pure and Ni-doped FeMnO₃ films selectivity plot, (b) 5-100 ppm ammonia concentration response curve of NFM2 film, (c) Response and recovery time of NFM2 for 50 ppm ammonia, (d) Different ammonia concentration response values of pure and Ni-doped FeMnO₃ films.

The ammonia-sensing characteristics of Ni-doped FeMnO₃ thin films with varying dopant concentrations were evaluated at room temperature. During the measurements, the baseline current of each sensor was allowed to stabilize before exposure to ammonia. Upon introducing ammonia at different concentrations, a clear change in the sensor current was observed, confirming the interaction between the gas molecules and the sensing surface[39]. The films

exhibited n-type semiconductor behaviour, as evidenced by a rapid increase in current upon ammonia injection. Selectivity towards ammonia, a reducing gas, is a vital performance parameter for the MOS-type gas sensor. Selecting a target gas from a pool of common interfering analytes is essential for real-world applications. The 3D bar graph shown in Figure. 11(a) illustrates the comparative responses of NFM0, NFM1, NFM2, and NFM3 films to 100 ppm of various gases, including acetone, 2-propanol, ethanol, 1-butanol, and Ammonia, at room temperature. The selectivity results clearly demonstrate that the NFM2 thin film exhibits the highest selectivity toward ammonia among the tested gases, indicating a strong preferential interaction between NH_3 molecules and the sensing surface. The enhanced selectivity toward ammonia can be attributed to the favourable adsorption of NH_3 molecules on oxygen-vacancy-rich active sites together with efficient charge transfer at the sensing surface. The optimised defect concentration introduced by Ni doping promotes selective interaction with ammonia molecules under ambient conditions. Furthermore, the current response (I_a) of NFM2 to ammonia was significantly greater than its response to other target gases. The selectivity (%) was calculated using Eq. 6 [40].

$$\text{Selectivity (\%)} = \left(\frac{S_x}{\sum S_t} \right) \times 100 \quad (6)$$

Here, $\sum S_t$ represents the sensor's overall sensitivity to all target gases. In contrast S_x refers to the specific sensitivity of the target gas. The selectivity (%) of the fabricated sensors for ethanol, acetone, 2-propanol, benzene, 1-butanol, and ammonia was approximately 3.6%, 4.6%, 7.4%, 4.9%, 2.8%, and 67%, respectively. Notably, the NFM2 sensor exhibited the highest selectivity (67%) towards Ammonia. Such variations in selectivity towards different gases typically arise from differences in charge-transfer interactions between gas molecules and the sensing layer, which influence the resulting electrical signal. Among the test samples, the NFM2 films exhibited exceptional ammonia selectivity, attributed to their strong interactions with ammonia molecules. This might be because adsorbed ammonia interacts strongly with the active sensing sites of the NFM2 layer. The enhanced ammonia response can also be explained by its relatively small molecular size and low dipole moment, which favour rapid diffusion and adsorption compared to other Volatile Organic Compounds. These attributes provide compelling evidence of the NFM2 sensor's superior gas-discrimination ability. The transient response behaviour of the Ni-doped FeMnO_3 thin film was systematically analysed at room temperature over an

ammonia concentration range of 5–100 ppm, as illustrated in Figure 11(b). The sensing response increases gradually with increasing ammonia concentration, indicating good linear behaviour over the investigated concentration range. The nearly linear increase in sensing response with ammonia concentration indicates excellent adsorption kinetics and stable charge-transfer behaviour within the investigated concentration range, demonstrating the reliability of the fabricated sensor for quantitative ammonia detection. The linear relationship between sensor response and ammonia concentration confirms the reliable detection capability of the fabricated Ni-doped FeMnO_3 sensor. The NFM2 film, in particular, exhibited a marked enhancement in sensing response and recovery upon exposure to 50 ppm of ammonia, demonstrating its improved sensing performance. This heightened sensitivity is largely attributed to its n-type semiconductor nature. As shown in Figure 11(c), the NFM2 film exhibited response and recovery times of approximately 136 and 94 seconds, respectively, at a 50 ppm ammonia concentration. The response process involves the diffusion of NH_3 molecules toward the sensing surface, followed by adsorption and subsequent surface reactions with chemisorbed oxygen species. These sequential processes require sufficient time, resulting in a response time of 136 s. In contrast, once the ammonia supply is interrupted, weakly adsorbed NH_3 molecules rapidly desorb from the sensing surface while atmospheric oxygen is immediately re-adsorbed, restoring the electron depletion layer. Consequently, the recovery process occurs more rapidly, producing a recovery time of 94 s. At higher ammonia concentrations, the collision frequency between NH_3 molecules and the sensing surface increases, thereby accelerating adsorption kinetics and facilitating faster establishment of the sensing equilibrium. Furthermore, among the tested films, NFM2 showed the greatest sensitivity compared to NFM0, NFM1, and NFM3, as shown in the Figure. 11(d). Notably, within the first minute of exposure to ammonia, the current surged by more than two orders of magnitude, exhibiting a rapid current response. This observation confirms the NFM2 sensor's high sensitivity at ambient temperature. The primary cause of this notable reaction is the nanostructured films' huge surface area, which encourages the adsorption of more reactive oxygen species. Furthermore, improved gas contact and diffusion are further supported by the NFM2 sample's increased surface roughness. Collectively, these findings highlight the promise of NFM2-based sensors for effective ammonia detection, particularly in environmental monitoring applications.

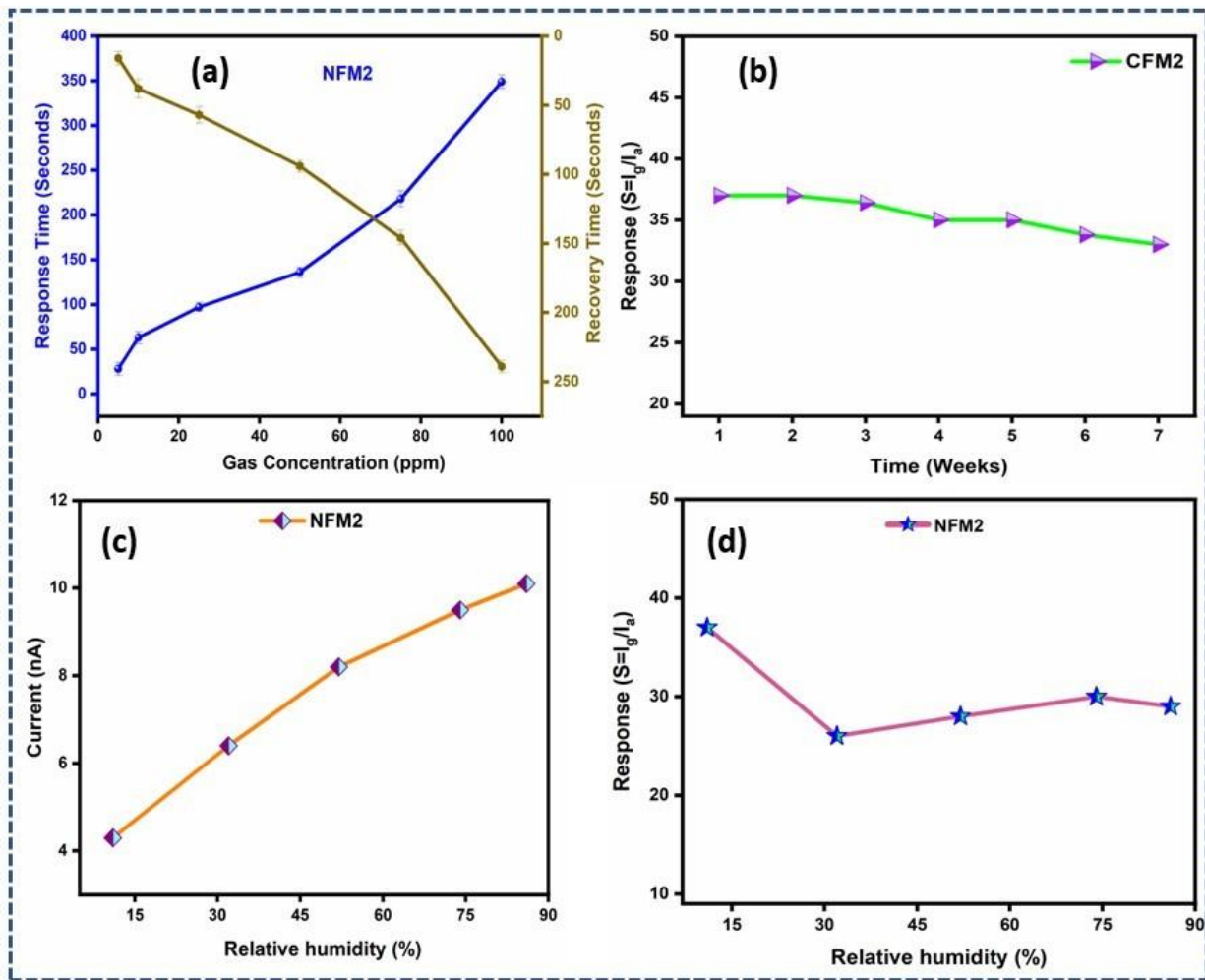


Figure 12. (a) Response and recovery time for NFM2 film of different ammonia concentrations, (b) stability of NFM2 for 50 ppm ammonia, (c) Baseline current of NFM2 film at different humidity atmospheres, (d) sensing performance of the NFM2 film towards 50 ppm ammonia under different humidity conditions.

Figure.12 (a) illustrates the response and recovery times of NFM0, NFM1, NFM2, and NFM3 films, measured at ammonia concentrations between 5 to 100 ppm. All the samples showed rapid recovery after the removal of ammonia gas. The rough surface morphology enhances the desorption of ammonia molecules from the film, enabling rapid recovery. Conversely, moderate response times are associated with slower adsorption of ammonia vapour onto the film surface at room temperature. Figure.12 (b) The stability performance of the

NFM2 sensor was monitored for seven weeks to evaluate its long-term reliability, with measurements taken weekly at 100 ppm of ammonia at ambient temperature. Because of its rough surface texture and improved surface area-to-volume ratio, which both increase the number of active sites and enhance gas-response performance, the results validated the NFM2 film's exceptional stability under ambient conditions. The excellent long-term stability demonstrates the strong adhesion of the sensing layer to the substrate. It confirms that Ni incorporation effectively maintains the structural and electrical integrity of the FeMnO_3 thin films during prolonged operation. Environmental Humidity was also found to play a crucial role in the operation of resistive-type sensors [41–43]. The presence of water vapour affects both the baseline current and the gas-sensing efficiency. A hygrometer connected to the sensing setup was used to test the NFM2 sensor at different relative humidity (RH) levels (11%, 32%, 52%, 74%, and 86%) to evaluate these impacts. LiCl , MgCl , $\text{Mg}(\text{NO}_3)_2$, NaCl , and KCl saturated salt solutions were used to provide controlled RH conditions. As depicted in Figure 12(c), the sensor's baseline current increased markedly with rising humidity, from 11% to 86% RH. Adsorbed water molecules are reported to cause this phenomenon by allowing proton conduction on the NFM2 surface. In humid conditions, adsorbed water molecules compete with ammonia molecules for active adsorption sites on the sensing surface. Consequently, a gradual decrease in the sensing response is observed as relative humidity increases due to competitive adsorption effects. Nevertheless, the sensor retains satisfactory sensing performance throughout the investigated humidity range, demonstrating good operational stability under practical environmental conditions. Figure 12 (d) depicts how the NFM2 sensor is currently responding to 50 ppm ammonia present in the atmosphere at different RH values. The sensor's reliability across various RH conditions was demonstrated by its consistent performance, with a variance of less than 40%. Sensor behaviour was also discovered to be influenced by the competitive adsorption of water and ammonia molecules. Ammonia facilitates charge transfer and modifies resistance through its interactions with surface oxygen species. However, at elevated humidity, excess water molecules may suppress gas adsorption, reducing sensitivity. Therefore, careful control and optimisation of humidity conditions are crucial to improving the real-world applicability of the NFM2 thin-film gas sensor. As shown in Table 3, the sensing response of the Ni-doped FeMnO_3 thin film is comparable to or exceeds that of several previously reported room-temperature ammonia sensors prepared using different

fabrication techniques. In particular, the NFM2 film exhibits a response of 67 to 100 ppm ammonia at ambient temperature, demonstrating competitive sensing performance among spray-coated metal oxide sensors.

Table 3

The gas-sensing behaviour of ammonia was compared with findings reported in the literature.

Materials	Methods	Operating Temperature (°C)	Ammonia Concentration (ppm)	Sensor response (I_g/I_a)	Reference
Ni–ZnO	Spray pyrolysis	Room Temperature	100	2.52	[44]
Fe ₂ O ₃	Thermal oxidation	250	100	18.8	[45]
Co–ZnO	Spray pyrolysis	Room Temperature	100	3.48	[46]
CuPC/ZnO	Solvothermal method	Room Temperature	100	15.8	[47]
ZnFe ₂ O ₄	Spray pyrolysis	Room Temperature	100	38.8	[48]
Ti ₃ C ₂ Tx/TiO ₂ /CuO	In situ oxidation method	Room Temperature	100	56.9	[49]
rGO/WO ₃	Hydrothermal	300	100	11	[50]
rGO–ZnO	Wet chemical method	Room Temperature	20	8.92	[51]
1.5 rGO/ZnO	Spray method	Room Temperature	10	1.20	[52]
Ti/Graphene	Chemical vapor deposition	Room Temperature	400	~7	[53]

Ni-FeMnO ₃	Spray pyrolysis	Room Temperature	100	67	This work
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In addition to the competitive sensing response, the proposed Ni-doped FeMnO₃ sensor offers several practical advantages, including room-temperature operation without external heating, low power consumption, simple spray pyrolysis fabrication, good humidity tolerance, and long-term operational stability. These characteristics demonstrate the proposed sensor's potential for portable ammonia sensing systems.

4. Ammonia sensing mechanism

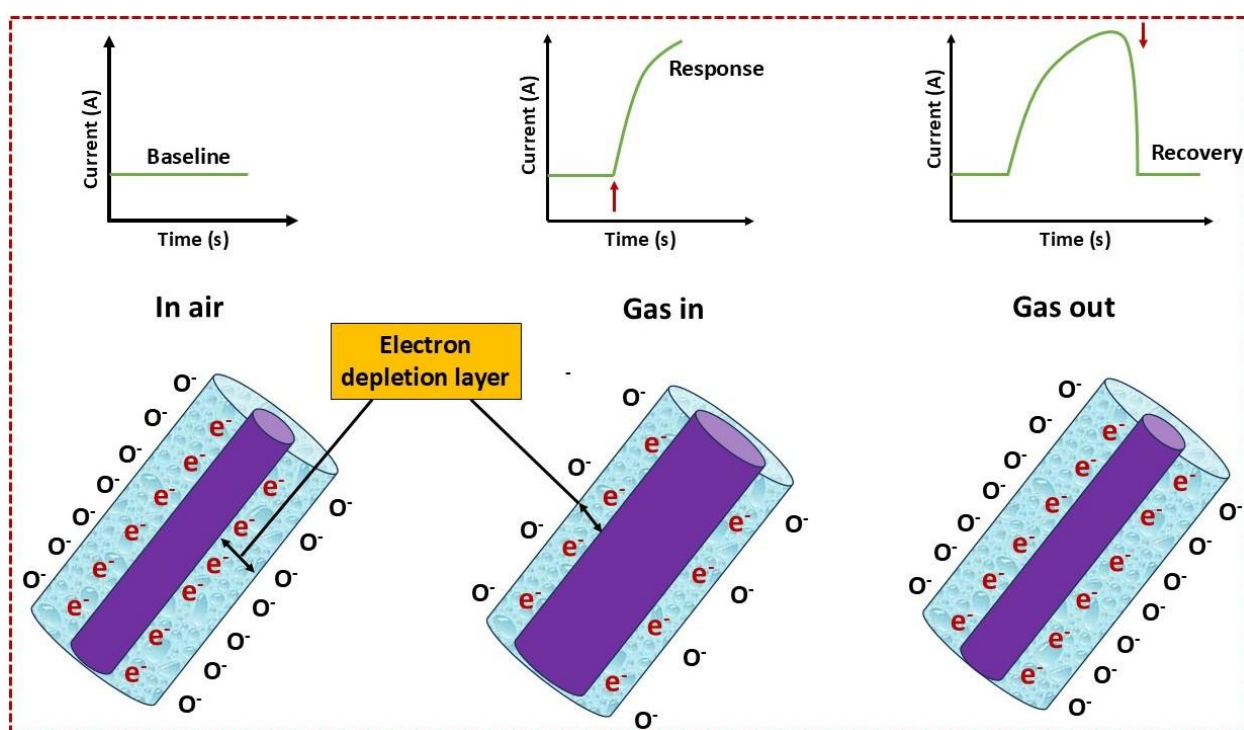


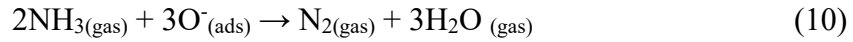
Figure 13. Ammonia sensing mechanism of Ni-doped FeMnO₃ films.

Figure 13 shows that the gas-sensing mechanism of the Ni-doped FeMnO₃ thin film for ammonia is primarily governed by changes in electrical resistance, driven by surface interactions between gas molecules and chemisorbed oxygen species. Due to its higher surface roughness, NFM2 exhibited the best ammonia-sensing performance among the four samples. High surface roughness increases the effective surface area of a film, providing many active sites for gas molecules to adsorb oxygen molecules. Atmospheric oxygen molecules are initially adsorbed on the surface of the FeMnO₃ thin film and subsequently capture electrons from the conduction

band, forming chemisorbed oxygen species such as O_2^- , O^- , and O^{2-} . This process creates an electron depletion layer near the surface of the sensing material. The oxygen adsorption process is represented by the following equations (7, 8, 9).



The surface of the NFM2 film, which facilitates the adsorption of NH_3 gas on oxygen-adsorbed sites, allows electrons to be transferred to the conduction band. This process reduces the thickness of the electron-depleted layer, lowering the resistance of the sensing film. Redox reactions are usually expressed by the equation (10).



The enhanced sensing characteristics of the NFM2 thin film originate from the synergistic effects of Ni-induced defect engineering. XPS analysis confirms an increased concentration of oxygen-vacancy-related species, AFM reveals enhanced surface roughness, while Hall-effect measurements demonstrate improved electrical transport. These structural and electronic modifications collectively increase oxygen adsorption, accelerate electron transfer during NH_3 adsorption, and ultimately enhance room-temperature sensing performance. The released electrons increased the material's conductivity, resulting in a measurable decrease in resistance. Nickel doping plays a crucial role in this mechanism by introducing additional active sites and oxygen vacancies [54]. Additionally, increasing the number of oxygen vacancies improves the catalytic activity of the $FeMnO_3$ sensing layer. The presence of oxygen vacancies promotes the adsorption of oxygen molecules, resulting in the formation of surface chemisorbed species O_2^- , O^- , and O^{2-} . The interaction of ammonia gas with these adsorbed oxygen ions releases electrons back to the conduction band. This electron-transfer process significantly increases the conductivity of the sensing film, resulting in a measurable change in electrical resistance. Therefore, the synergistic effect of Ni doping, increased oxygen vacancy concentration, and enhanced surface roughness leads to improved ammonia sensing performance by facilitating faster adsorption-desorption kinetics and enhanced electron transfer. This enhancement contributes to the increased sensitivity, faster response, and better selectivity towards ammonia.

gas in Ni-doped FeMnO₃ films. Therefore, the sensing enhancement observed in the NFM2 thin film cannot be attributed to a single factor but rather to the combined effects of an optimised microstructure, increased oxygen-vacancy concentration, improved electrical conductivity, and efficient charge-transfer kinetics introduced by Ni incorporation.

5. Conclusion

Ni-doped FeMnO₃ thin films were successfully synthesised by the spray pyrolysis method and systematically analysed for ammonia gas sensing at ambient temperature. The crystalline phase of FeMnO₃ was confirmed by structural analysis, and morphological analysis showed that, upon Ni incorporation, the porous nanostructures exhibited a higher surface roughness. Among the fabricated samples, the NFM2 thin film exhibited excellent sensing properties, with an ammonia selectivity of 67% at 100 ppm along with response and recovery times of 136 s and 94 s, respectively. The enhanced sensing properties are mainly due to the combined effects of optimised Ni doping, increased surface roughness, higher oxygen vacancy concentration, and improved charge transport in the sensing layer. Moreover, the sensor consistently reads 5 ppm of ammonia, indicating sensitivity to low gas levels. The observed room-temperature sensing ability indicates the potential of Ni-doped FeMnO₃ thin films for low-power, low-cost gas-sensing applications. These findings provide useful insights into the design of transition-metal-doped metal oxide thin films for effective ammonia sensing to monitor the environment and ensure safe operations in industry.

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