



Effect of Manganese Doping in SnO₂ Thin Films and its NO₂ Gas Sensing Performance

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ABSTRACT

By using an automated nebulizer spray pyrolysis technique with varied concentrations of manganese chloride (0 - 3%) in the spray solution of tin chloride, thin films of pure and manganese-doped tin oxides (Mn-SnO₂) were deposited. X-ray diffraction investigations indicated that 2% Manganese chloride concentration in the spray solution promoted development along (200) and (220) directions. The preferred growth direction in the (200) and (220) planes decreased with increasing manganese chloride doping concentration (2-3%) in the solution. The surface morphology of the films had changed as a result of adding Manganese as a dopant. Compositional analysis was carried out using EDAX. From UV-Vis spectroscopy, the optical properties of the SnO₂ and Mn-SnO₂ thin film were observed; the maximum optical absorbance was in the wavelength range of 300 - 400 nm. The concentration of Mn in the films affected the intensity of the photoluminescence emission peak detected at 347 and 392 nm for pure SnO₂ and Mn-SnO₂ films, respectively. The gas sensing performance of the films was examined by dynamic method against NO₂ gas, at an operating temperature of 250 °C and 400 ppm gas concentration. Mn-SnO₂ films achieved quick response and recovery times of 17 s and 34 s.

Keywords: Manganese doping; Thin films; Gas sensing; SnO₂; NO₂.

1. INTRODUCTION

In most solid-state gas sensors, thin films of polycrystalline semiconducting metal oxide materials like SnO₂ are utilized (Kiruthiga *et al.* 2022; Lee *et al.* 2000; Wang *et al.* 2010; Yamazoe *et al.* 1983; Yamazoe and Miura, 1992). The development in the properties of these materials has been the main focus of studies done in this area till now. The gas sensitivity of polycrystalline semiconductor metal oxide materials might be improved in a variety of methods nowadays; doping and adding more metals are the most efficient methods for achieving those goals (Cheng *et al.* 2021; Vijendra *et al.* 2020; Wang *et al.* 2020). The surface reactivity, adsorption and desorption characteristics of gas-sensing materials can be successfully modified by these metals, which are efficient catalysts. It was discovered that adding transition metals having the properties of noble metals to a gas sensing system can improve sensor response and selectivity, and help to increase sensitivity, reduce operating temperatures and other factors (Navale *et al.* 2021; Dayekh and Hussain, 2023; Basu and Basu, 2009; Ze *et al.* 2022). In addition, transition metals including Mn, Zn, Fe, W, Ni, Co, and Cr are excellent catalysts (Saruhan *et al.* 2021; Tomatis *et al.* 2018). According to research, adding transition metals as doping agents or even as an addition layer also enables modifying the electro-physical characteristics, structural characteristics, catalytic activity and adsorption characteristics of the doped and added material (Navale *et al.* 2021; Dayekh

and Hussain, 2023). Transition metals and metal oxides are therefore frequently used as catalysts in heterogeneous catalysis as well as doping components in the production of semiconductors (Korotcenkov *et al.* 2004; Lichen *et al.* 2018; Kanan *et al.* 2009). Even though transition metals have the potential to functionalize metal oxide characteristics that are essential in gas sensor applications, they are still used more rarely in gas sensors as transition metals (Choi *et al.* 2004; Kumar *et al.* 2009; Buvailo *et al.* 2010; Liua *et al.* 2010; Liu *et al.* 2015). Additionally, there is insufficient depth in the research on the gas-sensing characteristics of metal oxides doped with transition metals. An attempt has been made in this work to deal with initial changes in dopant to observe the performance of doped SnO₂ film for further research development.

2. EXPERIMENTAL DETAILS

Tin oxide films and manganese-doped tin oxide films were deposited using tin dichloride dihydrate (SnCl₂·2H₂O) and manganese chloride (MnCl₂), respectively. Double-distilled water and ethanol were mixed in a 3:1 combination. In this mixture, an accurately determined quantity of SnCl₂·2H₂O was added to create the precursor solution, which had a strength of 0.3 M. Then, the mixture was stirred in a magnetic stirrer until it became a clear precursor solution; subsequently, it was first transferred into a solution holder and then sprayed onto the hot substrate kept at the deposition temperature

of 450 °C using a thermocouple-based digital temperature controller. For manganese-doped tin oxide film, additionally, manganese chloride was added in ethanol, distilled water and tin dichloride mixture (Palanichamy *et al.* 2019; Mariappan *et al.* 2013; Kumar *et al.* 2017) with different doping percentages. The spray rate of the solution to the hot substrate was maintained at 0.1 ml/min throughout the experiment, the distance between the spray nozzle and the substrate was set at 10 cm, the pressure of the carrier gas was held at 0.2 Pa for both films and the coating volume was kept constant at 5 ml. After deposition, films were permitted to gradually cool at room temperature (Tamil *et al.* 2016).

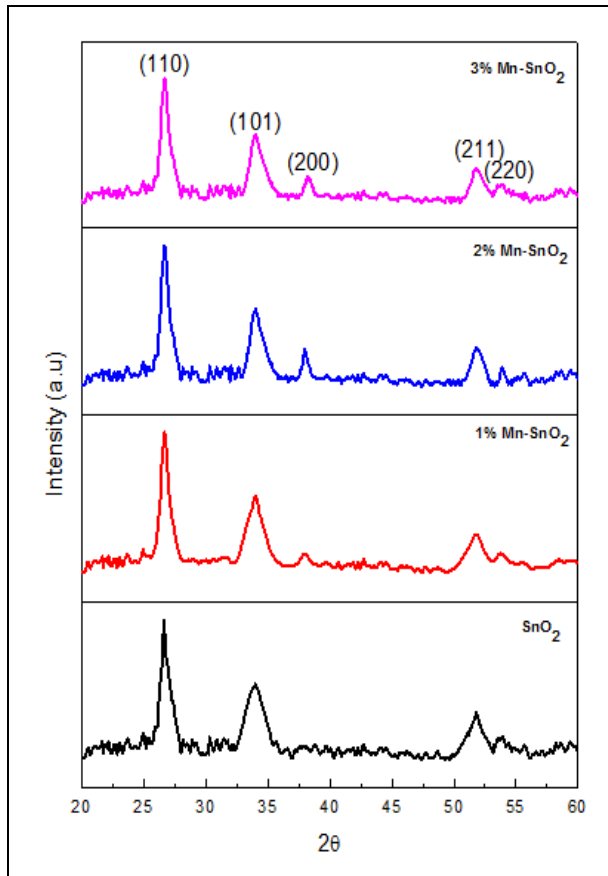


Fig. 1: XRD pattern of Pure SnO₂ and Mn-SnO₂ thin films

3. RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS

Fig. 1 depicts the XRD patterns of pure and different percentages of manganese-doped SnO₂ thin films. The JCPDS cards were used to identify the individual peaks, which are located at 2θ = 26.6°, 33.89°, 37.95°, 51.78° and 54.75°, respectively, with (h k l) values of (110), (101), (200), (211) and (220). The polycrystalline tetragonal rutile-type SnO₂ phase is observed in both instances, and the peak locations of the films are discovered to be in excellent agreement with JCPDS data card 41-1445. A strong influence on the

structural properties was observed when the doping concentration of Mn was increased as 2% in Mn-SnO₂ film. It was confirmed by the variation of diffraction pattern intensity.

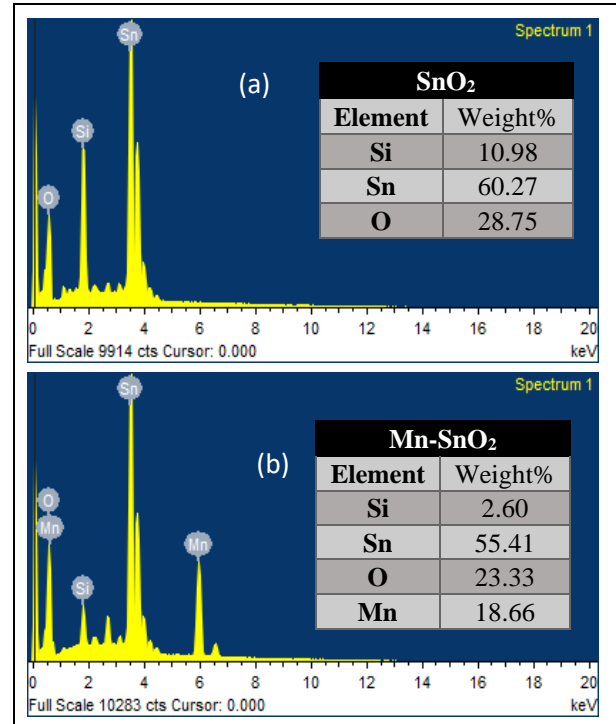


Fig. 2: (a & b) EDAX spectra of Pure and Mn-doped SnO₂ thin films

The particle size ranges between several nanometers. The determined grain size is shown in Table 1, and the FWHM of the diffracted peak was used to determine the strain and particle size.

The following equation was used to compute the lattice constants and average particle size (D) (Zoleikha *et al.* 2022),

$$D = \frac{k\lambda}{\beta \cos\theta} \dots\dots\dots (1)$$

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \dots\dots\dots (2)$$

where, d is the interplanar spacing, θ is the Bragg diffraction angle, β is the full width at half maximum (FWHM), and λ is the X-ray wavelength, which has a value of 1.542. The crystallite size is in the range of several nanometers according to Scherrer's equation. The following equations have been used to determine the lattice strain (ε) and dislocation density (δ) of pure and Mn-doped SnO₂ thin films (Vinila *et al.* 2022; Said *et al.* 2018),

$$\epsilon = \frac{\beta}{4 \tan \theta} \dots\dots\dots (3)$$

$$\delta = \frac{1}{D^2} \dots\dots\dots (4)$$

In Table 1, the estimated values for the microstructural parameters are given. Although the data in Table 1 for pure and different doping concentrations indicate different particle sizes, they are all at the nanoscale level. It further demonstrates that the value of dislocation density and strain for the various doping concentrations is due to an increase in the number of defects, which is favorable for gas sensing (Maheswari *et al.* 2020).

The *c/a* ratio for pure SnO₂ and Mn-doped SnO₂ films was found to increase (Table 1) up to 2% of Mn doping. Depending on the ionic radius and crystallinity of the dopant, the rise in lattice constant may result from an increase in the doping percentage of elements up to 2%, which will impact the original structure. As a result, there is a noticeable rise in the lattice constant, which supports the inclusion of the ions in the host lattice.

3.2 ELEMENTAL ANALYSIS

The quantitative analysis of the prepared thin films was carried out to determine the elemental composition between pure SnO₂ and Mn-SnO₂ films. Fig. 2 (a & b) shows the film composition which confirms the presence of Sn, O and Mn peaks in corresponding samples. The presence of silicon in the films was because of the usage of the glass substrate.

3.3 MORPHOLOGICAL STUDY

The surface morphology of the prepared films was analyzed by using a Field Emission Scanning Electron Microscope (FE-SEM) with ~5 K to ~100 K magnifications which are shown in Fig 3(a) to (b).

The particles were uniformly distributed with good surface coverage, had good crystallinity and a high magnification image revealed the presence of flax-like grains in pure SnO₂ film; whereas, Mn-SnO₂ film was seemingly found to have evenly coated spherical grains.

3.4 OPTICAL CHARACTERIZATION

The relationship between optical absorption and photon energy for films sprayed with a nebulizer atomizer is shown in Fig. 4. The films exhibit a rise in absorbance at wavelengths above 250 nm. The maximum absorbance intensity of the deposited films was recorded at the wavelength range from 315 nm to 350 nm.

Tauc plot was used to estimate the optical band gap energy (*E_g*). The optical absorption coefficient at the absorption edge for direct inter-band transition is given by,

$$(\alpha h\nu)^2 = A (h\nu - E_g) \dots\dots\dots (5)$$

where, *A* is the absorption constant for a direct transition, *h* is Planck's constant, *ν* is photon frequency and *E_g* is the optical band gap. (Kamble *et al.* 2017).

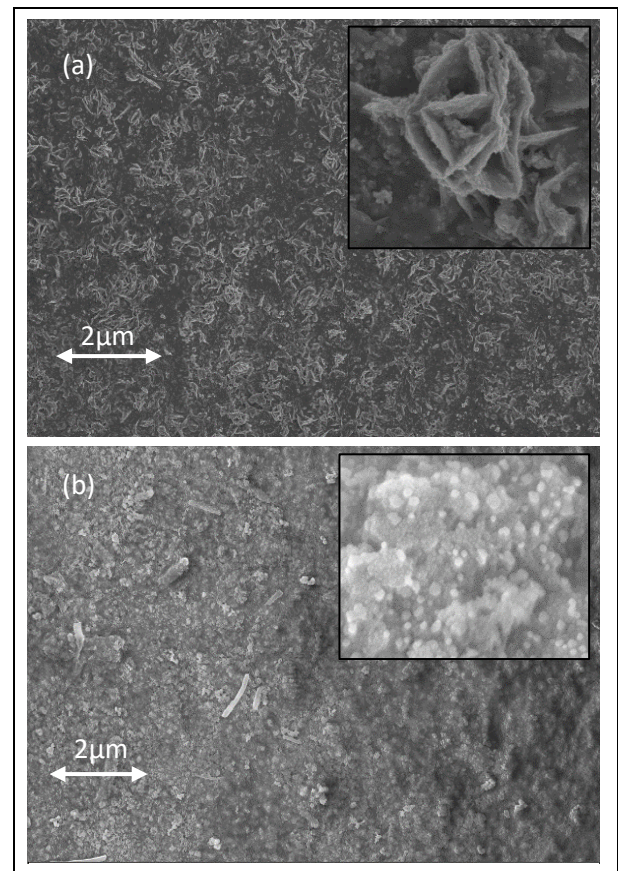


Fig. 3: (a & b) FESEM image of pure and Mn-SnO₂ thin films

By plotting $(\alpha h\nu)^2$ vs. $h\nu$ (inset of Fig. 4), the band gap for a direct allowed transition was determined. At ambient temperature, the UV band gap values of deposited films were 3.44 eV for pure SnO₂ and 3.23, 3.17 and 3.25 eV for Mn-doped SnO₂ films with concentrations of 1, 2 and 3%, respectively. Due to a reduction in particle size on Mn-SnO₂ thin films, the band gap value seemingly decreased for 1 and 2% of Mn-doped SnO₂ films (Aboud *et al.* 2019).

3.5 PHOTOLUMINESCENCE PROPERTIES

Photoluminescence (PL) measurement at room temperature was adopted to ensure the optical properties and the possible effect of Mn incorporation in doped SnO₂ films. Fig. 5 depicts the PL spectra of pure SnO₂ and Mn-SnO₂ thin film, which has the highest peak emission intensity wavelength at 347 nm and 392 nm for both pure and Mn-doped SnO₂ films as the excitation source with broad visible emission range from 325 - 450 nm. Due to the increase in oxygen vacancies in the Mn-doped SnO₂ film, the PL peak intensity increased for 0-2% Mn concentration. As a result of the decrease in grain size, the oxygen vacancy ratio increased in the

manufactured Mn-doped SnO₂ thin film, which raised the PL intensity of the doped films (Azam *et al.* 2012).

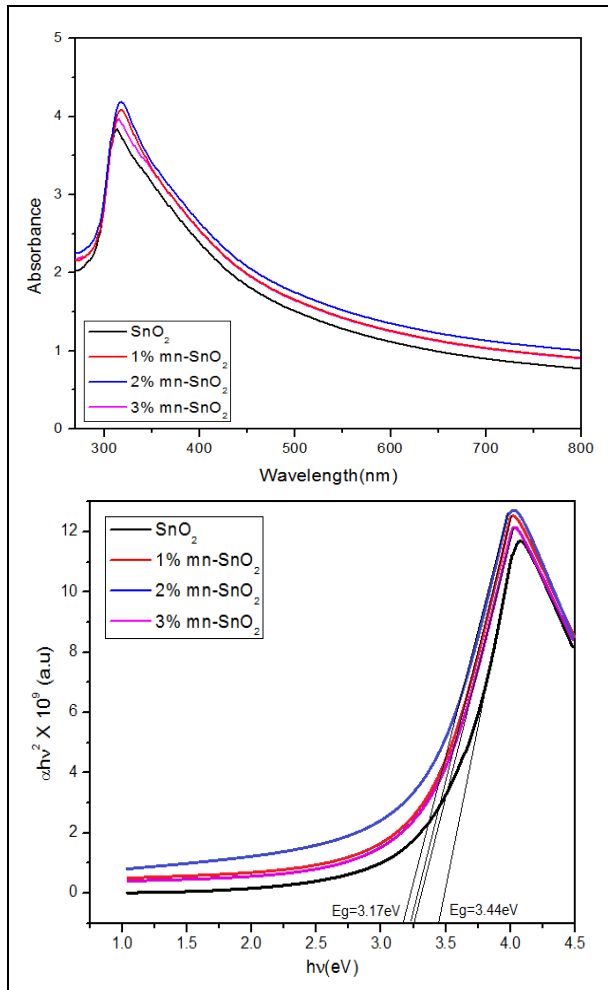


Fig. 4: UV-Vis spectra of Pure and Mn-SnO₂ thin films

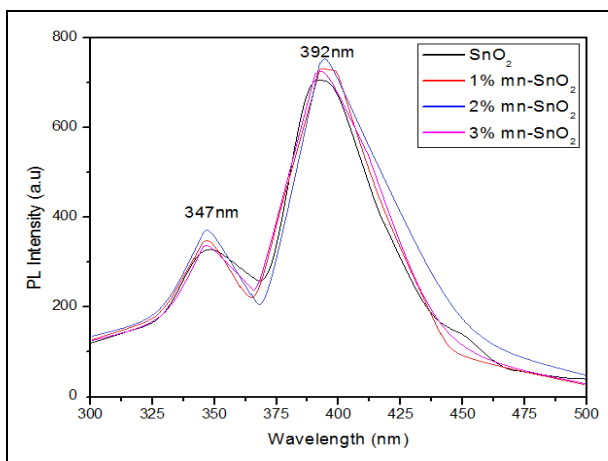


Fig. 5: PL spectra of Pure and Mn-SnO₂ thin films

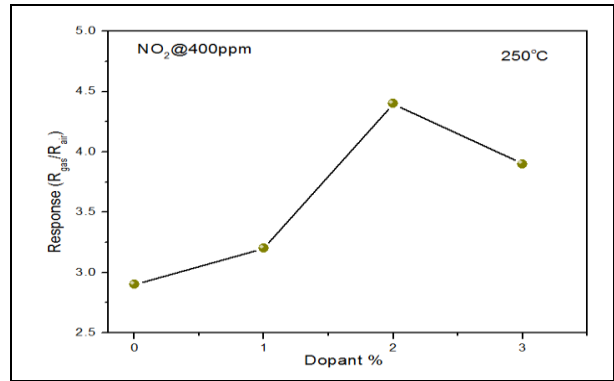


Fig. 6: Response graph of 0-3% Mn-SnO₂ thin films

3.6 SENSOR RESPONSE

The dynamic gas sensing assembly carried out the investigations on the gas response of pure and Mn-doped SnO₂ thin films against NO₂ gas at operating temperatures of 250 °C in 400 ppm of gas concentration. The semiconducting thin-film metal oxide gas sensors were deeply investigated (Guan *et al.* 2020).

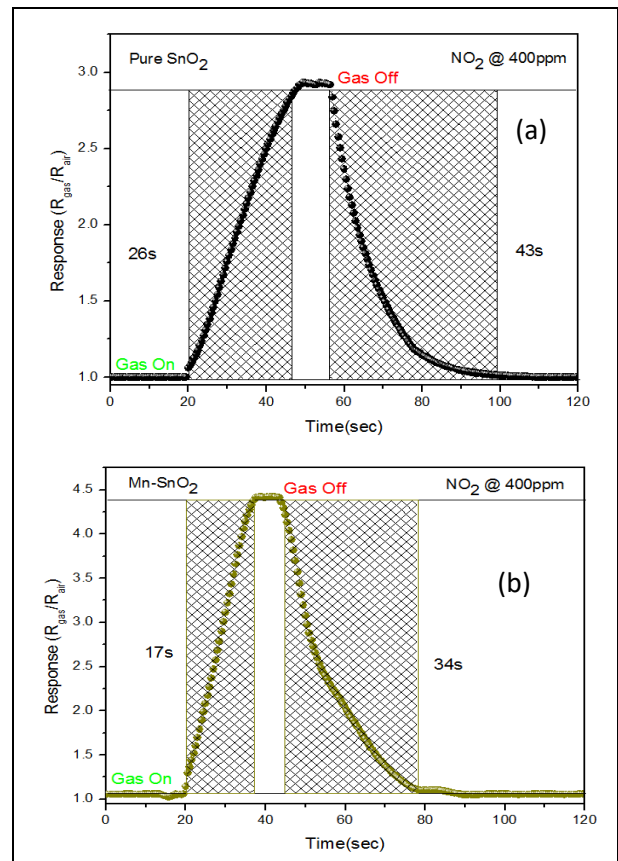


Fig. 7: (a & b) Response and recovery time of Pure and Mn-SnO₂ thin films towards NO₂ gas

The gas response is influenced by factors including structure, concentrations, film thickness, morphology and operating temperatures. In this present work, the gas response towards NO₂ gas for pure SnO₂ and Mn-doped SnO₂ thin films was examined. The response graph of SnO₂ films doped with 0-3% Mn is

shown in Fig. 6. However, 2% Mn-doped SnO₂ thin film exhibited an impressive reaction towards NO₂ gas with 400 ppm of gas concentration when operated at 250 °C. It has been discovered that when compared to pure SnO₂, 2% Mn-SnO₂ exhibited a stronger sensitivity towards NO₂ gas (Salah *et al.* 2020).

Table 1. Calculated grain sizes of SnO₂ and Mn-SnO₂ thin films

Name of the thin film samples	Lattice Constant(Å)		Thickness of the film (µm)	Particle size (nm)	Dislocation Density (x 10 ¹⁵) lines. m ⁻²	Strain (x10 ⁻³)
	a	c				
SnO ₂	4.7031	3.1733	119.5	56.66	0.312	20.21
1%Mn-SnO ₂	4.7044	3.1773	120	55.13	0.329	20.43
2%Mn-SnO ₂	4.7110	3.1802	120	42.02	0.566	24.65
3%Mn-SnO ₂	4.7093	3.1781	120	43.32	0.533	22.37

Table 2. NO₂ gas sensing performances of various SnO₂-based thin films

Material	Fabrication method	Op. temperature/NO ₂ concentration	Response	t _{res} /t _{rec}	Reference
“SnO ₂ –NiO	“Sputtering	“200°C/10 ppm	“2.25 (R _g /R _a)	-	(Jose <i>et al.</i> 2020)
SnO ₂ –MoO ₃	Sol–gel	170°C/500 ppm	3.75 ((R _g –R _a)/R _a)	2s/ -	(Kaur <i>et al.</i> 2010)
SnO ₂ –In ₂ O ₃	FSP method	250°C/50 ppm	~3 (R _g /R _a)	2s/3mns	(Inyawilert <i>et al.</i> 2015)
SnO ₂ –SnO	Sputtering	60°C/10 ppm	4.35 ((I _g –I _a)/I _a)	165s/329s	(Jeong <i>et al.</i> 2018)
SnO ₂ –Ag ₂ O”	Sputtering”	275°C/10 ppm”	5.91 (R _g /R _a)”	28s/168s	(Yuan <i>et al.</i> 2022)
SnO ₂ :WO ₃	Thermal evaporation	250°C/220ppm	~550 ((R _g -R _a)/R _a)	2s/120s	(Haidar <i>et al.</i> 2018)
Zn ₂ SnO ₄	Spray pyrolysis	200 °C /200ppm	3.31 (R _g /R _a)	25s/221s	(Ganbavle <i>et al.</i> 2014)
ZnSnO ₃	Spray pyrolysis	RT/80ppm	12.05 ((R _g -R _a)/R _a)	169s/217s	(Dabbabi <i>et al.</i> 2019)
CdS-SnO ₂	Chemical Solution Deposition	RT/10ppm	377.7 (R _g /R _a)	8s/107s	(Ajay <i>et al.</i> 2022)
SnO ₂ -Pd	Flame Chemical Vapor Deposition	30°C/10ppm	12.35 (R _g /R _a)	~300s/750s	(Myung <i>et al.</i> 2021)
B-doped CNTs/SnO ₂	CVD	RT/500ppb	0.91 ((R _g -R _a)/R _a)	1min/2.5hours	(Leghrib <i>et al.</i> 2011)
Ni- SnO ₂	Electrospinning	200 °C/20 ppm	180.7 (R _g /R _a)	24 s /35 s	(Wen <i>et al.</i> 2017)
Ag-SnO ₂ /rGO	Sol-gel	RT /50ppm	2.13 (R _a /R _g)	35s/ -	(Wenqian <i>et al.</i> 2021)
Sb-doped Zn ₂ SnO ₄	Sputtering	600°C/300ppm	4 (R _g /R _a)	-	(Yamada <i>et al.</i> 1998)
Mn-SnO ₂	Automated Nebulizer Spray Pyrolysis	250°C/400ppm	4.4 (R _g /R _a)	17s/34s	This work

3.7 RESPONSE AND RECOVERY TIME

Fig. 7 (a & b) displays the response and recovery time of pure and Mn-SnO₂ thin films for 400 ppm of NO₂ gas at 250 °C. It has been noted that the Mn-SnO₂ thin film sensor responded to NO₂ gas at a maximum time of 17 s and recovered in 34 s, owing to the presence of a doping element with a good percentage (Sureshkumar *et al.* 2019). For pure SnO₂ film, 26 s and 43 s of response and recovery times were observed, respectively.

Table 2 can be used to compare the gas response results of the present investigation against the results of other investigations. The sensor performance results in the current work demonstrated an improvement in rapid response and recovery times and sensor response value. The optimal doping percentage is realized as the response reached 4.4 at 400 ppm of NO₂ gas with very quick response and recovery times of 17 s and 34 s, respectively. This illustrates that 2% of Mn-doped SnO₂ thin film has great potential to be a promising NO₂ gas sensor.

4. CONCLUSION

Using an automated nebulizer spray pyrolysis technique, thin films of pure SnO₂ and Mn-SnO₂ were deposited on the glass substrate. XRD, EDAX, FESEM, UV-visible spectroscopy, PL characteristics and gas sensor performance were used to characterize the prepared thin films. The XRD spectra of all samples exhibited tetragonal rutile-type SnO₂ phases, and the peak position of the films was found to be in good match with JCPDS data. Due to doping, the average crystallite size decreased. The homogeneous dense nanoparticles that developed on the substrate were seen in the FE-SEM image of the pure and Mn-SnO₂ thin films. As compared to pure SnO₂ thin films, the band gap energy values for Mn-SnO₂ thin films were lower. The concentration of doping affects the PL intensity. 2% Mn-doped SnO₂ thin film has shown the strongest response to NO₂ gas at a working temperature of 250 °C, as well as a quick reaction and rapid recovery times. Therefore, it might be concluded that Mn-SnO₂ thin films would be effective NO₂ gas sensors. The focus shall be laid upon 2% Mn-SnO₂ films for further research of SnO₂-based thin film works.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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