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Optimized Spray Pyrolysis Route for Mn_3O_4 Thin Film Synthesis

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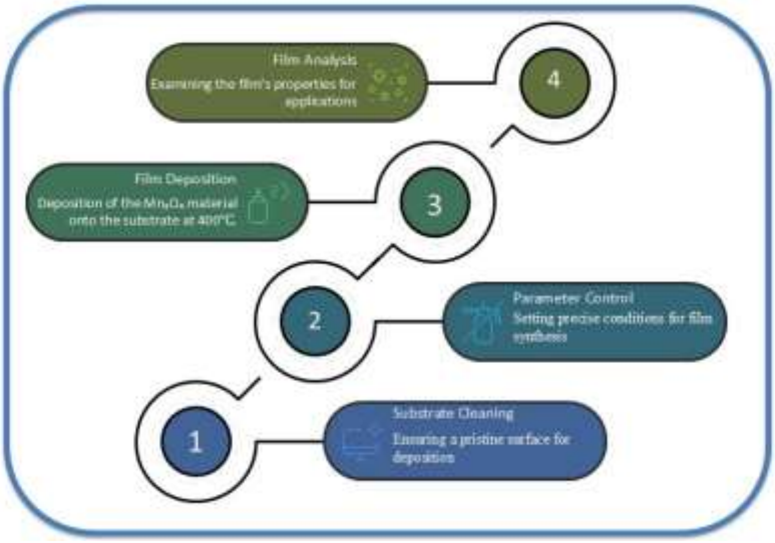
ABSTRACT

Thin films of Nanocrystalline Mn_3O_4 were synthesized on meticulously cleaned glass substrates at 400℃ via spray pyrolysis method. The deposition parameters were a precursor volume 20mL, compressed air pressure of 30psi, nozzle to substrate distance of 30 cm, and spray rate 2mL/min. The X-ray diffraction confirmed the formation of pure-phase Hausmannite Mn_3O_4 exhibiting tetragonal spinel structure. The band gap of 2.58eV was determined from UV–Visible spectroscopy and it is consistent with previous study literature reports for this phase. The results highlight the effect of substrate preparation along with controlled and optimized spray pyrolysis parameters in depositing a fine Mn_3O_4 thin films.

Graphical Abstract:-



Introduction

The tuneable spinel tetragonal lattice and the co-existence of different oxidation states ((Mn^{2+}, Mn^{3+}) has made Mn_3O_4 a significant material for its catalytic, electrochemical and magnetic properties[1–4]. Promising functionalities of Mn_3O_4 nanostructured thin films have been seen in areas like gas sensing, solar energy harvesting and energy storage. In the process of deposition of thin films via spray pyrolysis facilitates the scalable, cost-effective and simple route which also allows compositional and morphological regulation over large-area substrates [5,6].

Substrate temperature, spray rate, precursor concentration, substrate surface cleanliness and atomizing gas pressure are the major parameters which influence the film quality and determine the crystallinity, phase formation and optical behaviour. Spray pyrolysis is a premier route for the formation of nanostructured metal oxide films as it provides compositional control, scalability and balances cost efficiency. In spray pyrolysis method, the precursor solution vaporizes on a heated substrate following the nucleation and growth processes resulting in the crystallized oxide film. Though some of the previous studies have systematically analysed the united impact of rigorous substrate cleaning protocol and optimized deposition parameters for Mn_3O_4 thin films via spray pyrolysis route.

This work focuses on the Mn_3O_4 thin films by spray pyrolysis at 400 °C on rigorously cleaned glass substrates. Its Optical and structural characterization demonstrates the formation of tetragonal Hausmannite Mn_3O_4 and the energy band gap is nearabout the previously studied reports[1], which ensures the reproducibility of functional manganese oxide films.

Materials and Methods

Substrate Cleaning

Glass slides were exposed to a multistep cleaning protocol. Substrates were washed detergent wash, ultrasonic acetone bath, extended chromic acid treatment for 24 hours, and multiple rinses with double-distilled water. This rigorous surface preparation lessened contaminants that badly impact film nucleation and uniformity.

Precursor Solution

Aqueous solution of manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) was prepared in 20 mL double-distilled water with 0.1M concentration. The solution was stirred magnetically for 10 minutes to ensure homogeneity.

Spray Pyrolysis Deposition

The precursor solution was spray-deposited on glass substrates heated at 400 °C using a pneumatic atomizer. The spray rate was maintained at 2 mL/min, with atomizing air pressure at 30 psi and nozzle-to-substrate distance fixed at 28 cm. Deposition proceeded until full solution delivery, after which the films were cooled to room temperature in ambient atmosphere.

Results and Discussion

Structural Characterization

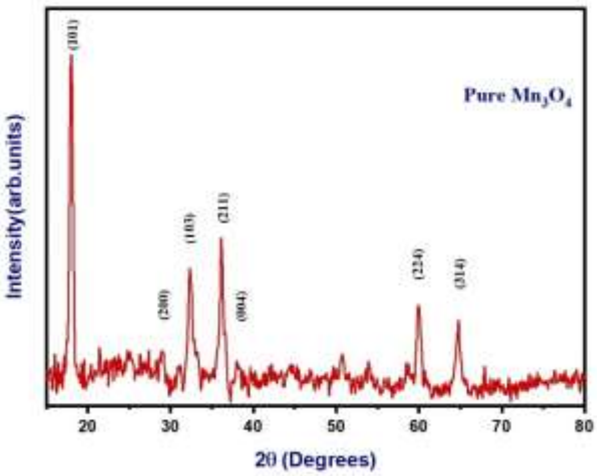


Fig. 2: - X-ray diffraction pattern of Pure Mn_3O_4 thin films

X-ray diffraction patterns (Fig. 2) validated the successful formation of the Hausmannite Mn_3O_4 phase, a tetragonal spinel structure which matches with JCPDS Card No.00-001-1127 [7]. Significant diffraction peaks were observed which are indexed to planes (101), (200), (103), (211), (004), (224), and (314). These peaks demonstrated the high crystallinity and phase purity. Also, the absence of additional peaks exhibits no secondary phases which is well aligned with previously studied literature[1,4,8]. To determine the average crystallite size, the Debey-Scherrer's equation was used.

$$D = \frac{k\lambda}{\beta cos\theta},$$

where D is the average crystallite size, $k(0.9)$ is the shape factor [9], λ is the X-ray radiation wavelength (1.5406 Å), β is the full-width half maxima, and θ is Bragg's angle of diffraction[10]. The values of crystallite sizes, lattice parameters[11], strain, distortion parameter, dislocation density, and stress can be observed in Table 1.

Sr. No.	D(Crystallite Size) (nm)	Dislocation Density (10^{16} lines. nm^{-1})	Strain	Lattice Parameters		Volume ($Å^3$)	u Parameter	Distortion Parameter
				a=b (Å)	C (Å)			
1	13.2278	0.1442	0.0171	5.7548	9.4361	312.5116	0.3739	0.639668

Table 1 Crystallite size, dislocation density, strain, lattice parameters, Volume, u Parameter, distortion parameter values of Pure Mn_3O_4 thin films

Optical Properties

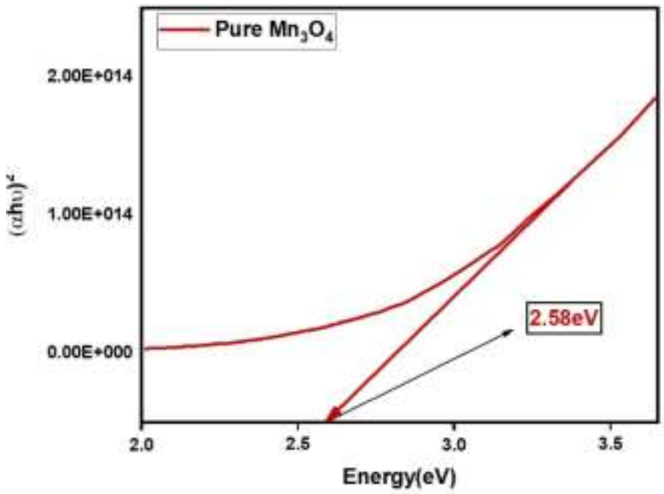


Fig.3:-Energy band gap curve of Pure Mn_3O_4 thin films

The optical absorption spectrum of Mn_3O_4 thin film in the wavelength range 200–1000 nm has been studied. UV–Visible spectroscopy (Figure 3) revealed an optical band gap (E_g) of 2.58 eV for the Mn_3O_4 thin films, consistent with Hausmannite Mn_3O_4 films reported in previous studies. The band gap was calculated using Tauc's plot reflecting a direct allowed transition[1,9].

Conclusions

On rigorously cleaned glass substrates and heated to 400 °C, nanocrystalline Mn_3O_4 thin films with a well-defined Hausmannite tetragonal structure were successfully synthesized via spray pyrolysis. XRD characterization established phase-pure Mn_3O_4 formation, additionally optical spectroscopy demonstrated an energy band gap near 2.58 eV, confirming the semiconducting nature of the films. The results highlight the critical importance of systematic substrate cleaning and control over spray pyrolysis parameters to comprehend consistent, homogeneous thin films suitable for optoelectronic and catalytic functions. These results contribute to advancing scalable fabrication techniques for functional manganese oxide nanomaterials.

References:-

1. Dahamni, M. A. et al. Spray pyrolysis synthesis of pure and mg-doped manganese oxide thin films. Coatings 11, (2021).

2. Vignesh, R., Sivakumar, R. & Sanjeeviraja, C. A detailed analysis on optical parameters of spinel structured Mn3O4 thin films deposited by nebulized spray pyrolysis technique. Opt Mater (Amst) 111, (2021).

3. Li, N. et al. Efficient removal of chromium from water by Mn3O4@ZnO/Mn3O4 composite under simulated sunlight irradiation: Synergy of photocatalytic reduction and adsorption. Appl Catal B 214, 126–136 (2017).

4. Ibrahim, A. Y. & Hammoodi, F. G. Structural and Optical Properties of Mn3O4:NiO Nanostructure Thin Films Prepared by Chemical Spray Pyrolysis Method. Journal of Nanostructures 15, 229–238 (2025).

5. Tomar, M. S. & Garcia, F. J. SPRAY PYROLYSIS IN SOLAR CELLS AND. Crystal Growth Charact vol. 4 (1981).

6. Moses Ezhil Raj, A. et al. XRD and XPS characterization of mixed valence Mn 3 O 4 hausmannite thin films prepared by chemical spray pyrolysis technique. Appl Surf Sci 256, 2920–2926 (2010).

7. Atique Ullah, A. K. M. et al. Oxidative Degradation of Methylene Blue Using Mn3O4 Nanoparticles. Water Conservation Science and Engineering 1, 249–256 (2017).

8. Barreto, J. et al. Structural Characterization of Mn3O4(001) Thin Films and Their Interaction with CO. Journal of Physical Chemistry C 128, 14972–14977 (2024).

9. Dubal, D. P. et al. A novel chemical synthesis of interlocked cubes of hausmannite Mn3O4 thin films for supercapacitor application. J Alloys Compd 484, 218–221 (2009).

10. Lokhande, S. D., Awale, M. B. & Mote, V. D. Optical and gas sensing properties of Cu-doped ZnO nanocrystalline thin films for sensor applications. Journal of Materials Science: Materials in Electronics 33, 25063–25077 (2022).

11. Chouchaine, A. et al. SYNTHESIS, CHARACTERIZATION OF MN3O4: ADSORPTION APPLICATION AND ANTIBACTERIAL EVALUATION. J. Chil. Chem. Soc vol. 67 (2022).