Synthesis and Structural Characterization of As-Deposited and Annealed MnO Thin Films Prepared by SILAR Method

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ABSTRACT

Manganeses Oxide was coated on glass substrates using a SILAR process at 100 deposition cycles in this study. To further understand the structural and morphological behaviour of the produced samples, X-ray diffraction and scanning electron microscopy were used to characterize them. The thickness of the films was also calculated.

Keywords: XRD, SEM, SILAR, Thickness

1. INTRODUCTION

Historically Bunsen and Grove first obtained thin metal films in a vacuum system in 1852. The limit of thickness varied from a nano meter to a few micro meters depending upon the field of application.[1] Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry, which are based on characteristic of the thickness, geometry, and structure of the film. At the initial stages, investigation on the thin films was made out of scientific curiosity, particularly for their significantly different properties from those of the same material in bulk form.[2] However, the acquired capability of controlling properties of the thin films in subsequent years, helped immensely the use of thin films in electronic optoelectronics and other devices and as a result the electronics industry has become the greatest beneficiary of thin film technology.[3]

In this work, MnO thin films were coated by SILAR method and its structural properties and thickness were studied.

2. MATERIALS AND METHODS

Silar method has been chosen in this work as it is inexpensive, simple and capable of deposition of optically smooth uniform and homogenous layers[4].Mno thin films were coated by Silar method using glass subtrates. Before deposition, subtrates were cleaned in ethanol. Later they were rinsed with distilled water.

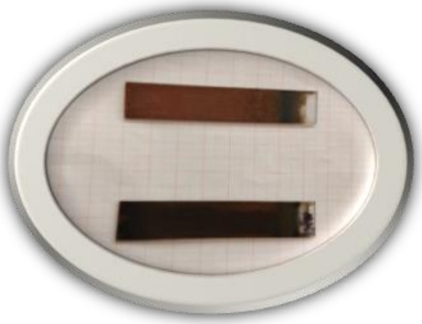

Fig 2.1 Image of As- Deposited and Annealed Mno Thin films

For this deposition, cationic precursor was prepared by dissolving 0.1M of Manganese (II) chloride tetrahydrate and 4g of sodium hydroxide in 100ml of distilled water.The glass substrates were cleaned by using an ultrasonicator.The glass substrates were dipped into solution of Manganese (II) chloride tetrahydrate for 20s.It was then immersed in distilled water for 10s.Then it was immersed in NaOH for 20s followed by again dipping in distilled water. This formed one SILAR deposition cycle.Films were deposited by repeating SILAR cycles for 100 cycles. The prepared sample was annealed for 300 degrees Celsius in muffle furnace for two hours.The crystallographic properties were investigated by XRD (XPERT-PRO).The morphology of the films wasanalysed using SEM (ZEISS).

3. RESULTS AND DISCUSSION

The structural characterisation and thickness of MnO thin films are thoroughly explored.

3.1 XRD Analysis for Structural Characterization

The XRD patterns of MnO thin films were explored in depth in structural characterisation. [5]Using a CuKα radiation source and an XPERT – PRO diffractometer, the XRD patterns of the deposited MnO films were examined in theregion of 20° to 80° with a 0.0170 step size. 30 mA and 40 KV were the accelerating voltage and emission current, respectively.

To study the structural properties of the deposited MnO thin films X-ray diffraction (XRD) study was carried out. Fig 3.1,3.2 show the XRD pattern of MnO deposited by SILAR Method for 100deposition cycles for two samples respectively. The observed XRD pattern show the prominent peak at (220) [6]plane orientation for both the as deposited and annealed films prepared by 100 deposition cycles. However all diffraction Peaks of the MnO thin film correspond to the characteristic cubic structure of MnO thin films. The observed ‘d’ values were compared with standard ‘d’ values using joint Committee on Powder Diffraction Standards (JCPDS card no 24-0734).

The crystallite size of thin films were calculated from XRD patterns by using Scherrer's formula given below

$$D = k\lambda / \beta \cos\theta$$

Where,

D = Crystallite size

K = Constant

β = Corrected FWHM of the most intense peak

θ = Braggsangle Using these formula grain sizes can be determined.

The dislocation density has been calculated using crystallite size, by the equation

$$\text{Dislocation} = 1/D^2$$

The microstrain has been calculated by the given formula,

$$\text{Microstrain} = \beta \cos\theta/4$$

The lattice parameter calculated for MnO by the given formula

$$1/(d_{hkl}^2) = (h^2 + k^2 + l^2) * 1/(a^2)$$

The lattice parameter has been calculated and reported. The grain size, [7]dislocation density, micro strain [10]and lattice spacing[11] of MnO thin film for both as deposited and annealed films for 100 deposition cycles have been given below. For both the films prominent peaks were obtained at (103), (211) and (220).

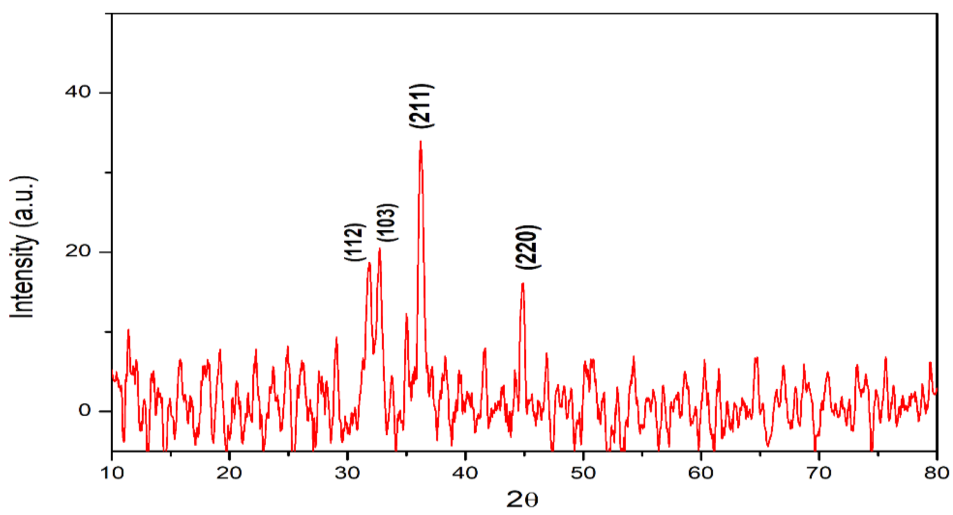

Fig 3.1 XRD pattern of As- Deposited MnO thin film

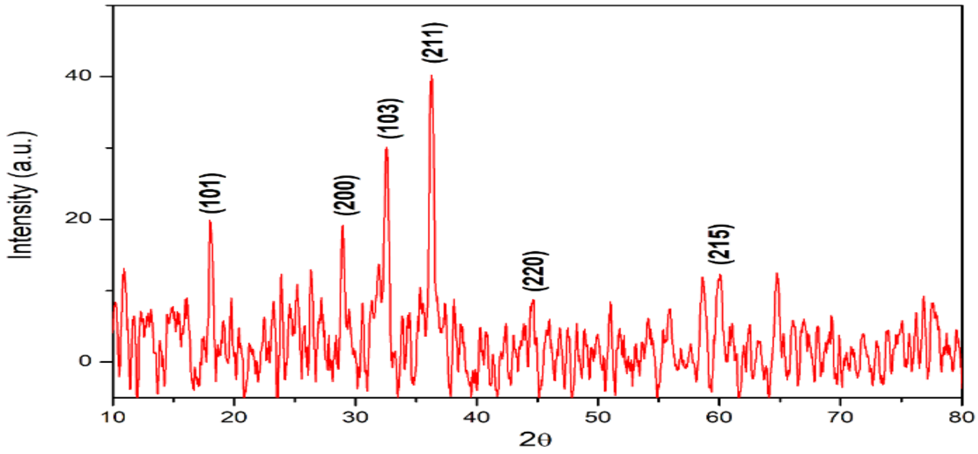

Fig 3.2 XRD pattern of Annealed MnO thin film

TABLE 3.1 For As Deposited MnO Thin Film

hkl	2θ	FWHM (β)	Grain Size(D) nm	Dislocation Density $10^3 nm^{-2}$	micro strain 10^{-3}	Lattice constant (a=b=c)
112	31.7	0.5	17.24	3.36	2.10	5.562
103	32.9	0.61	14.41	4.81	2.57	
211	36.3	2.9	10.38	9.28	2.03	
220	44.8	0.5	17.94	3.11	2.02	

TABLE 3.2 For Annealed MnO Thin Film

Hkl	2θ	FWHM (β)	Grain Size(D) nm	Dislocation Density $10^3 nm^{-2}$	Micro strain 10^{-3}	Lattice constant (a=b=c)
101	18.2	0.3	27.99	1.28	1.29	5.615
200	29	0.4	21.42	2.18	1.69	
103	33	0.5	17.30	3.34	2.09	
211	36.1	0.5	17.45	3.29	2.08	
220	45	0.4	22.44	1.99	1.61	
215	60	0.7	13.68	5.34	2.65	

3.2 SEM Analysis for Structural Characterisation of MnO Thin Films

SEM images of as deposited and annealed MnO thin films were found .They provide detailed views of surfaces of the object at very high magnification[8] .SEM Images involves analyzing the structures, textures[13] and features visible in the images to understand the morphology, composition and characteristics of the MnO sample.[9]The materials properties such as its microstructures, surface roughness,[12] porosityare also determined. Fig 3.3 and 3.4 show the SEM images of as deposited and annealed MnO thin films.

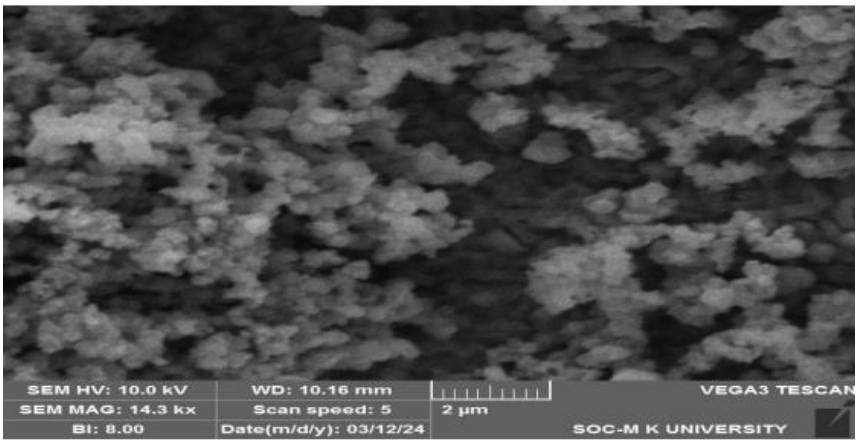

Fig3.3 SEM Image of as deposited MnO Thin Film

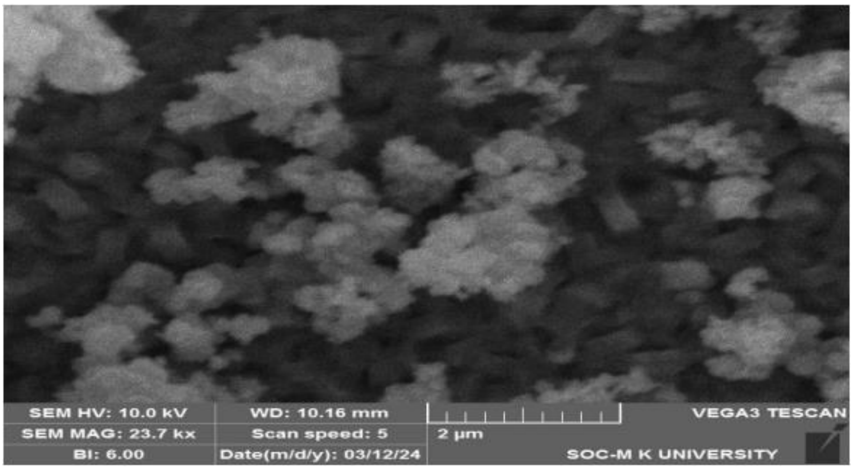

Fig 3.4 SEM Image of annealed MnO Thin Film

3.3**Thickness Measurement**

In the present study thickness measurement were done by the weight gain method for 100 deposition cycles .

$$t=m/ (A\,\rho)$$

where

m- mass of the coating

A- area of the film coated

ρ- Density of film (Mno)

TABLE 3.3 Thickness Measurement of as deposited and annealed MnO Thin Films

Sample Name	Deposition cycles	Thickness(microns)
MnO (as deposited)	100	0.003806
MnO (annealed)	100	0.0015

4. CONCLUSION

MnO thin films have been examined structurally and the film thickness has been calculated. The films deposited at 100 cycles are fairly homogeneous and polycrystalline, according to SEM analysis. The existence of Mn and O inthe produced MnO thin films was confirmed by papers. MnOhas good application as a supercapacitor. This would be confirmed by optical and electrical studies in future.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. APA Mondal, S. & Mitra, P. (2012). Effect of Manganese Incorporation in ZnO Thin Films Prepared by SILAR. J. Sci. Soc, 10, 139.

2. Bayram, Özkan, et al. "The role of cobalt doping on the optical and structural properties of Mn304 nanostructured thin films obtained by SILAR technique" Superlattices and Microstructures 128 (2019): 212-220.

3. Yu, Xin, et al. "Influence of S/Mn molar ratio on the morphology and optical property of y-MnS thin films prepared by microwave hydrothermal" Joumel of alleys and compounds 549 (2013) 15

4. Gopi, Chandu VVM, et al. "A strategy to improve the energy conversion efficiency arid stability of quantum dot-sensitized solar cells using manganese-doped cadmium sulfide quantum dots" Dalton Transactions 44.2 (2015) 630-638

5. Jadhav, P. R., et al. "Manganese oxide thin films deposited by SILAR method for supercapacitor application." A/P Conference Proceedings Vol 1536 No 1. American Institute of Physics, 2013

6. Gulen, Y, et al. "Fabrication and characterization of Mn-doped CuO thin films by the SILAR method" Ceramics International 396 (2013) 6475-6480

7. Belkhedkar, M. R., and A. U. Ubale "Physical properties of nanostructured Mn304 thin films synthesized by SILAR method at room temperature for antibacterial application" Joumal of Molecular Structure 1068 (2014) 94-100

8. Desai, Mangesh A., et al. "An investigation of chemical and electrochemical conversion of SILAR grown Mn304 into MnO2 thin films." Journal of Environmental Management 299 (2021). 113564

9. Balamurali, S., Chandramohan, R., Suriyamurthy, N. Parameswaran, P. Karunakaran, M., Dhanasekaran, V. & Mahalingam, T. (2013). Optical and magnetic properties of Mn doped ZnO thin films grown by SILAR method Joumal of Materials Science Materials in Electronics, 24, 1782.

10. Dubal, D P, et al. "A novel chemical synthesis and characterization of Mn304 thin films for supercapacitor application" Applied Surface Science 256.14 (2010): 4411-4416

11. Beknalkar, S. A., et al. "Supercapacitive Performance of SILAR Grown Mn_3O_4 Nanoclusters: Effect of Cationic Precursor Concentration." *Chinese Journal of Physics* 72 (2021): 145-158.

12. Devi, K. Rathi, et al. "Role of dipping cycle on Mn doped ZnO thin films prepared by successive ionic layer adsorption and reaction method." *Sensor Letters* 17.12 (2019): 987-990.

13. Mishra, R. K., et al. "Influence of electrodeposition modes on the electrochemical performance of MnO_2 films prepared using anionic MnO_4^-(Mn^{7+}) precursor." *Ceramics International* 44.5 (2018): 5710-5718.