

Effect of film thickness on properties of SILAR deposited manganese oxide thin films

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Abstract

Manganese oxide is considered as one of the most attractive compound among the manganese oxide phases due to its fundamental chemical and physical properties, its use in energy-storage devices, electrochemical applications, and sensors. In this work, nanocrystalline manganese oxide thin films of different thicknesses were deposited on a FTO coated glass substrate by a simple chemical method (successive ionic layer adsorption and reaction, SILAR) based on alternate dipping of the substrate in of manganese sulphate and sodium hydroxide solution and rinsing between every immersion cycle with double distilled water (DDW). The structural study by XRD indicates that the films consist of nanocrystalline tetragonal phase. The particle size of spherical/cubic particles was found to be in the range 10–50 nm. The band gap energy was decreased with increase in film thickness. Change in surface architecture resulted into smaller surface wettability in thick film compared to thin one.

Keywords: Manganese oxide, SILAR, Film thickness, Spherical/cubic nanostructure, Superhydrophilic

I. INTRODUCTION

Manganese oxide has been thoroughly investigated owing to its important application in electrochemical capacitors [1], lithium batteries [2], electro catalysis for oxygen reduction [3] and MnO₂-based sensors for carbohydrates [4]. The high-surface and large-sized manganese oxide nanostructures is one of the most promising materials as active electrode material in pseudo capacitors, as its pseudo-capacitance arises from the III/IV oxidation state change at the surface of manganese oxide nanostructures [5]. Various conventional methods are known for forming manganese oxide thin films viz. microwave irradiation [6], hydrothermal [5], chemical vapour deposition [7], sputtering [8] etc. Keeping drawbacks of physical methods in mind recently, much emphasis has been put on the soft solution chemical processes for the preparation of advanced inorganic materials such as perovskite-type oxides [9], spinel-type oxides [10], nanotubes [11], nanowires [12] and nanodots [13] with quantized size. These low cost processes have

used environmentally benign conditions. Chemical methods such as chemical bath deposition method (CBD) [14], successive ionic layer adsorption and reaction method (SILAR) [15] electrodeposition [16] etc. are simple, economic and convenient for the deposition of large area metallic oxide thin films. These are low temperature methods and hence avoid oxidation and corrosion of the substrates. The preparative parameters such as concentration, pH, nature of the complexing agent, temperature etc. are easily controllable.

In CBD, the film formation on substrate takes place when ionic product exceeds solubility product. However, this results into precipitate formation in the bulk of solution, which cannot be avoided. This results in unnecessary formation of precipitation and loss of material. This drawback is greatly reduced by using a simple chemical deposition method i.e. successive ionic layer adsorption and reaction method (SILAR) [17].

The SILAR method is relatively a new and less investigated method, which is based on sequential reaction on the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and solvated ions in the solution. SILAR method has its own advantages such as layer-by-layer growing mode, excellent material utilization efficiency and good control over the deposition process along with the film thickness and large-scale deposition capability on any type of substrate. Any insoluble surface to which the solution has free access will be a suitable substrate for the deposition. As the deposition is carried out at or close to room temperature, it avoids oxidation or corrosion of metallic substrates. The facts affecting the growth phenomena are the quality of the precursor solutions, their pH values, concentrations, counter ions, individual rinsing and dipping times. In addition, complexing agent and pre-treatment of the substrate have been shown to affect the SILAR growth. These preparative parameters are easily controllable to obtain good quality of films, better orientation and improved grain structure.

In this investigation, attempt has been made to employ a SILAR method to deposit nanocrystalline manganese oxide thin films with different film thickness by changing deposition cycles. Preparative parameters are

optimized to get nanocrystalline thin films at relatively low temperatures. A further study has been made for the structural, surface morphological, band gap and wettability properties of the manganese oxide thin films by using X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption and water contact angle techniques, respectively.

II. EXPERIMENTAL DETAILS

2.1 Preparation of manganese oxide

Analytical reagent manganese sulfate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) and sodium hydroxide (NaOH) was used for the deposition of manganese oxide thin films. The cationic precursor was 0.2 M manganese sulfate. The source of oxide ions was 0.5 M NaOH. Prepared solutions were taken into beakers and for rinsing purpose ample quantity of distilled water were used. After every ten deposition cycles the water for rinsing was replaced. Deposition of manganese oxide thin films were carried out onto cleaned FTO coated glass substrates having sheet resistance $10\text{--}20 \Omega/\text{cm}^2$. FTO coated glass substrates were cleaned ultrasonically for 15 min first in acetone and then in water: isopropyl alcohol (1:1) solution and then rinsed with double distilled water. The cleaned FTO substrates were immersed in 0.2 M manganese sulfate for 20 s. The Mn^{2+} ions were adsorbed to the substrate. The substrates were then rinsed with double distilled water for 20 s to remove the desorbed ions. In the next step, the anions from anionic precursor (NaOH) maintained at temperature of 333 K solution are introduced to the system, which get reacted with the pre-adsorbed cations (Mn^{2+}) to form manganese oxide on the FTO substrate. In the last step, excess and unreacted species from diffusion layer are removed by rinsing the substrates in double distilled water for 20 s. By repeating such SILAR deposition cycles for several times, we have obtained homogeneous, well adherent, compact and secularly reflecting manganese oxide thin films of different thickness on FTO coated glass substrate. The colour of the film was found to be brownish. The darkness of brownish colour increases with increase in film thickness. A SONY high-resolution digital camera took colour photographs of the three samples of manganese oxide thin film. The physical properties of the manganese oxide films were investigated by X-ray powder diffractometer (XRD) (Philips, PW-3710). For the SEM analysis, manganese oxide thin films were coated with a 10 nm platinum layer using a Polaron scanning electron microscopy (SEM) sputter coating unit E-2500, before taking the image. The TEM micrograph was obtained with Philips CM-30 TEM unit (Point resolution = 2.4\AA) with acceleration voltage of 300 KV coupled with EDAX-DX-4 analyser. The optical absorption spectrum in the range 300–800 nm was recorded using UV–vis spectrophotometer. Contact angle measurement was based on the sessile-drop method consisting of the observation of water drop through a comparing microscope coupled to a goniometer (Phoenix

150, Surface Electro Optics, Korea). Two millilitre drops were deposited at different positions on the film surface using a Rame–Hart Inc. model-10 micro-syringe. Contact angle measurement was carried out at 30 s after the deposition of water drop on the film. This time is necessary for focusing and adjusting the crosshairs of the microscope on the drop.

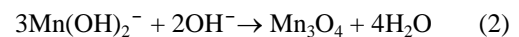
III. RESULTS AND DISCUSSION

3.1 Growth mechanism

Manganese oxide thin films were prepared by alternate immersing FTO coated glass substrate in separately placed cationic and anionic precursors with rinsing between every immersion. The growth kinetics of a thin film deposition process is ion-by-ion growth mechanism, which involves the ion-by-ion deposition at nucleation sites on the immersed surfaces. The mechanism of manganese oxide film formation by SILAR method can be explained as follows. Manganese sulphate is dissolved in double distilled water which gives manganese hydroxyl $\text{Mn}(\text{OH})_2^-$ ions.



When substrate is immersed in this solution, $\text{Mn}(\text{OH})_2^-$ ions gets adsorbed onto the substrate due to attraction between ions in the solution and surface of the substrate. These forces may be cohesive forces or Van der Waals forces or chemical attractive forces. Further reaction is followed by the immersion of substrate in NaOH anionic solution, where the chemical reaction between OH^- and $\text{Mn}(\text{OH})_2^-$ ions leads to the deposition of adherent manganese oxide layer.



Manganese oxide thin films are uniform and well adherent to the FTO coated glass substrate. After 95 deposition cycles, a slight decrease in film thickness was observed. This is possibly due to formation of an outer porous manganese oxide layer. Estimated thicknesses calculated from SEM imaging were $0.9 \mu\text{m}$, $1.8 \mu\text{m}$ and $2.6 \mu\text{m}$.

3.2. Structural studies

Manganese oxide is normal spinel oxide which is room temperature stable structure with Mn^{3+} in the octahedral positions and Mn^{2+} in the tetrahedral positions of the spinel structure. Fig. 1 shows the XRD patterns of manganese oxide thin films deposited for different thicknesses as $0.9 \mu\text{m}$, $1.8 \mu\text{m}$ and $2.6 \mu\text{m}$ with nomenclatures a, b and c, respectively. The planes corresponding to (1 1 2), (1 0 3) are in good agreement with JCPDS 24-0734, confirming the formation of Mn_3O_4 compound. The small peak intensities in XRD pattern revealed the existence of nanocrystalline crystallites [18]. Decrease in peak intensities with increase in number of deposition cycles in XRD patterns revealed the existence of nanocrystalline crystallites.

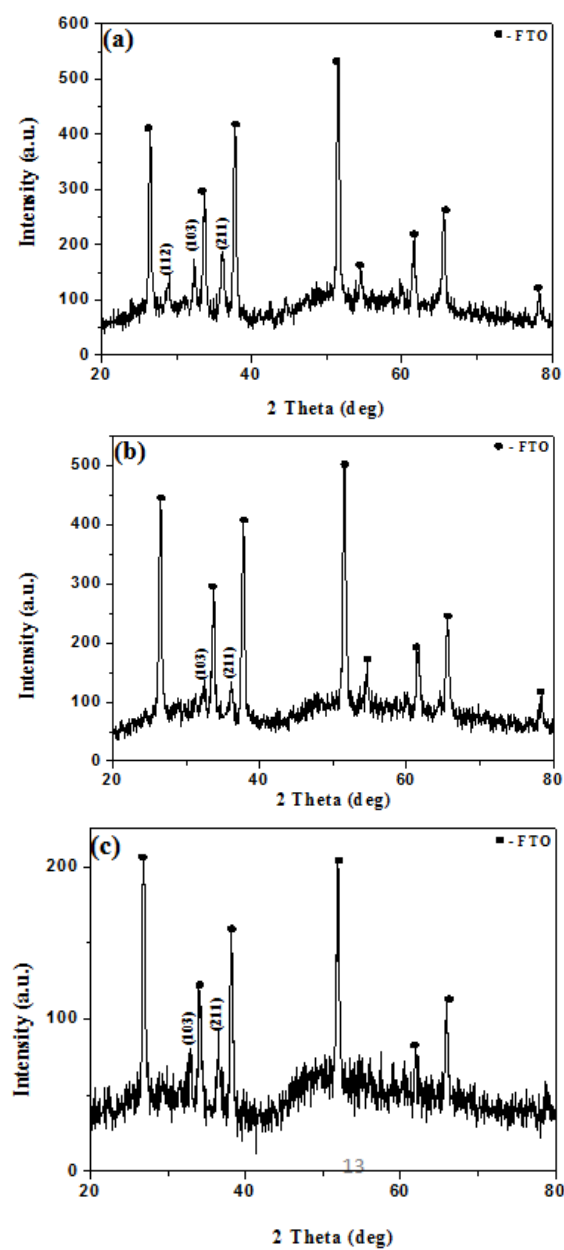


Figure 1 XRD patterns of manganese oxide thin films

3.3. Surface morphological studies

The surface morphological characterization highlighted the importance of film preparation in maintaining a nanostructured phase. Surface morphological studies of the manganese oxide thin films onto FTO coated glass substrates with different thicknesses has been carried out using SEM images and are shown in Fig. 2 (a-c). A well covering and smooth manganese oxide thin films surface can be seen. The increase in film thickness with number of deposition cycles is obvious. When the deposition cycles increases from 55 to 95 cycles, the diameter of particles increases as seen in the Fig. 2(a-c). The particle morphology observed was either spherical/cubic with uneven shapes. Since smaller grains tend to have surfaces

with sharper convexity, they gradually disappear by feeding the larger particles, as thickness increases [19]. Insets of Fig. 2(a-c) shows the colour changes with manganese oxide films thickness from brownish to dark brownish as thickness increases. The morphology of the crystals were not clear, TEM analysis was carried out.

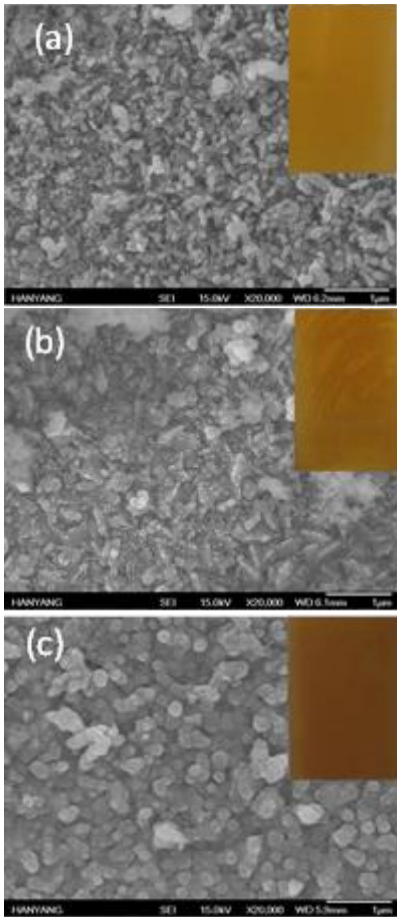


Figure 2 SEM images of manganese oxide thin films

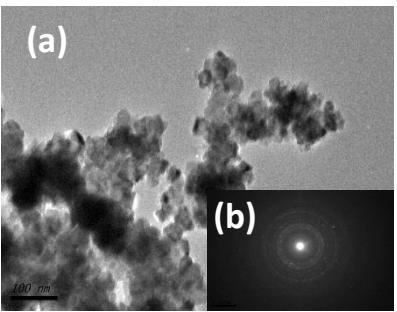


Figure 3 TEM image of manganese oxide thin film

Transmission electron microscopy is a primary method used to determine the accurate crystallite size. Fig. 3(a) shows the TEM picture of manganese oxide film at 2.6 μm film thickness which consisted mainly of spherical/cubic

particles. The particle size of spherical/cubic particles was found to be in the range 10–50 nm. Similar type of morphology has been reported Apate et al. [20] by microwave irradiation method. The corresponding selected area electron diffraction (SAED) pattern presented in Fig. 3. (b) shows evidence of nanocrystalline manganese oxide thin film of tetragonal hausmannite structure.

3.4 Optical absorption studies

The variations of optical absorbance (αt) of manganese oxide films for different thicknesses are shown in Fig. 4 (A). This spectrum reveals that manganese oxide film has high absorbance of light in the visible region, indicating applicability as an absorbing material. This data was further used for analysing optical direct band gap energy using following classical relation for near edge optical absorption in semiconductor.

$$\alpha = a (h\nu - E_g)^{n/2} / h\nu \tag{3}$$

where ‘ a ’ is a constant, E_g is the semiconductor band gap energy and ‘ n ’ is a number equal to 1 for the direct band gap and 4 for the indirect gap semiconductors.

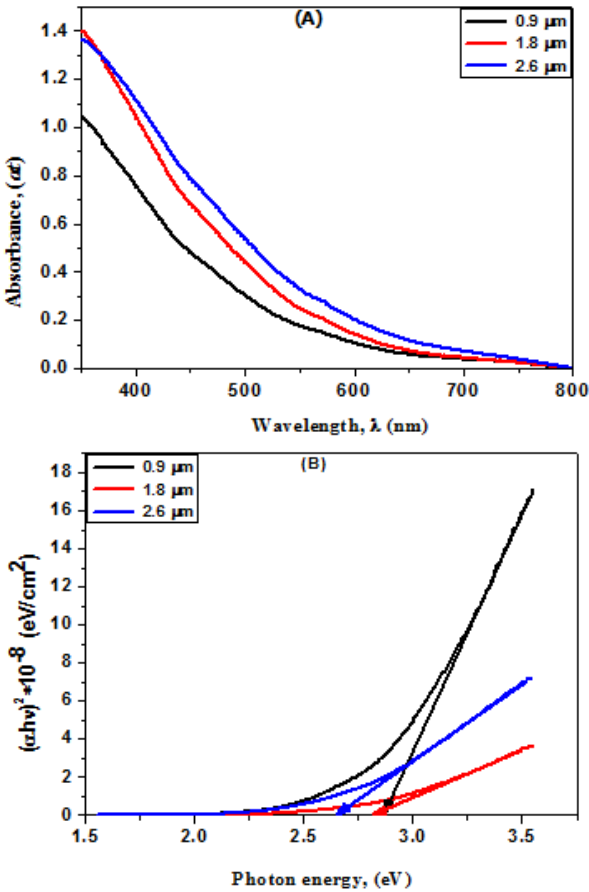


Figure 4 Variations of absorbance vs wavelength (A) and $(\alpha h\nu)^2$ vs $h\nu$ (B) of manganese oxide thin films

It is seen from the graph that optical absorption decreases with increase in the film thickness. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ are plotted [Fig.4(B)] for estimating the value of direct band gap energy of manganese oxide films by extrapolating curves to zero absorption coefficient. The decrease in direct band gap energy (2.88 to 2.64 eV) with increase in film thickness is confirmed, similar to the reports for optical absorption-thickness variation [21].

3.5 Wettability studies

The wetting behaviour is characterized by the value of the contact angle, a microscopic parameter. If the wettability is high, contact angle (θ), will be small and the surface is hydrophilic. On the contrary, if the wettability is low, (θ) will be large and the surface is hydrophobic. The contact angle is an important parameter in surface science and its measurement provides a simple and reliable technique for the interpretation of surface energies. The Young’s equation related the three interfacial tensions and the contact angle in a solid–liquid–vapor system is given by as

$$T_{lv}\cos\theta = T_{sv}-T_{sl} \tag{4}$$

where T_{lv} is the liquid–vapor surface tension, T_{sv} the solid–vapor surface tension, T_{sl} the solid–liquid surface tension and θ is the Young’s contact angle. The method involves the measurement of contact angle between water and the thin film. The contact angle is expected to depend upon local inhomogeneity, chemical composition and the surface morphology of the semiconducting electrodes. A contact angle of 0° means complete wetting, and a contact angle of 180° corresponds to complete non-wetting. Both super-hydrophilic and super-hydrophobic surfaces are important for practical applications [22].

Fig.5 (a-c) shows images of water contact angle measurement on manganese oxide surface as function film thickness and was 13.3° , 7.7° and 4.4° , respectively. The manganese oxide surface seems to be more water loving i.e. super-hydrophilic. Surface wettability was decreased with increase in film thickness due to relatively less internal and external strain energies compared to the thin one [23]. It is well known that in the electrochemical super capacitor, hydrophilic surface of the electrode is an essential factor for better performance [24].

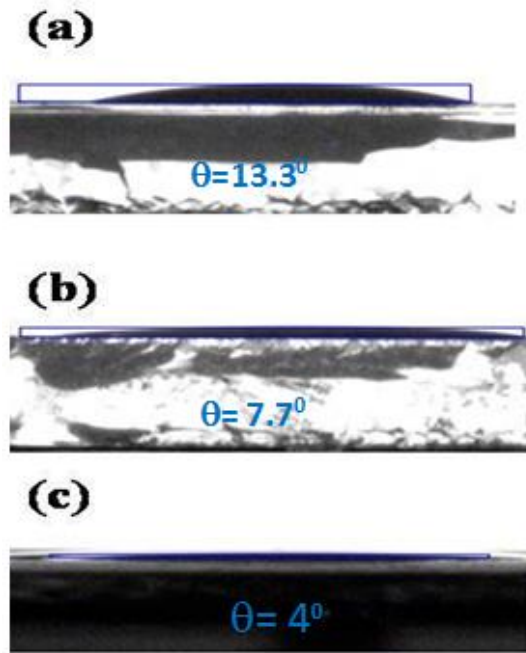


Figure 5 Water contact angle measurement of manganese oxide thin films

IV. CONCLUSIONS

Manganese oxide thin films have been successfully synthesized on to FTO coated glass substrate at relatively low temperature by changing number of deposition cycles. XRD pattern revealed that manganese oxide thin film exhibits tetragonal hausmannite structure. From morphological studies it is seen that manganese oxide thin films were smooth, unequal spherical/cubic grains which increase with film thickness and well covered to the FTO coated glass substrate with. The direct band transition was confirmed from optical absorption. The band gap energy was decreased with increasing film thickness. All films were hydrophilic in nature. This unique architecture of manganese oxide films may find a potential application in electrochemical supercapacitor. Efforts are in progress to study the electrochemical properties of manganese oxide thin films synthesized by SILAR method.

REFERENCES

- [1] S. Devaraj, N. Munichandraiah, *Electrochem. Solid State Lett.* 8 (2005) A373.
- [2] J.Y. Luo, J.J. Zhang, Y.Y. Xia, *Chem. Mater.* 18 (2006) 5618.
- [3] M.S. El-Deab, T. J. Ohsaka, *Electrochem. Soc.* 153 (2006) A1365.
- [4] G. Furlani, F. Pagnanelli, L. Toro, *Hydrometallurgy* 81 (2006) 234.
- [5] N. Wang, H. Pang, H. Peng, G. Li, X. Chen, *Cryst. Res. Technol.* 44 (2009) 1230.
- [6] Z. Fan, Z. Qie, T. Wei, J. Yan S. Wang, *Mater. Lett.* 6 (2008) 3345.
- [7] X. Huang, C. Pan, X. Huang, *Mater. Lett.* 61 (2007) 934.
- [8] P. Fau, J.P. Bonino, A. Rousset, *Appl. Surf. Sci.* 78 (1994) 203.
- [9] C.D. Lokhande, T.P. Gujar, V.R. Shinde, R.S. Mane, S.H. Han, *Electrochem. Comm.* 9 (2007) 1805.
- [10] J.L. Gunjekar, A.M. More, K.V. Gurav, C.D. Lokhande, *Appl. Surf. Sci.* 254 (2008) 5844.
- [11] X. W. Lou, D. Deng, J. Y. Lee, J. Feng, L. A. Archer, *Adv. Mater.* 20 (2008) 258.
- [12] X. Teng, W. Han, W. Ku, M. Hücker, *Angew. Chem. Int. Ed.* 47 (2008) 2055.
- [13] S. Acharya, U. K. Gautam, T. Sasaki, Y. Bando, Y. Golan, K. Ariga, *J. Am. Chem. Soc.* 130 (2008) 4594.
- [14] Deshmukh S. G., Panchal A. K., Kheraj Vipul, *AIP Conference Proceedings* 1728 (2016) 020023.
- [15] A.M. More, J.L. Gunjekar, C.D. Lokhande, O.S. Joo, *Appl. Surf. Sci.* 255 (2009) 6067.
- [16] T.P. Gujar, V.R. Shinde, S.S. Kulkarni, H.M. Pathan, C.D. Lokhande, *Appl. Surf. Sci.* 252 (2006) 3585.
- [17] H.M. Pathan, C.D. Lokhande, *Bull. Mater. Sci.* 27 (2004) 85.
- [18] D.P. Dubal, D.S. Dhawale, R.R. Salunkhe, S.M. Pawar, V.J. Fulari, C.D. Lokhande, *J. Alloys Comp.* 484 (2009) 218.
- [19] R.R. Salunkhe, C.D. Lokhande, *Sens. Actuator B* 129 (2008) 345.
- [20] S.K. Apathe, S.D. Naik, R.S. Sonawane, B.B. Kale, Neela Pavaskar, A.B. Mandale, B.K. Das, *Mater. Res. Bull.* 41 (2006) 647.
- [21] L.D. Kadam, P.S. Patil, *Mater. Chem. Phys.* 68 (2001) 225.
- [22] R.D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, K. Hashimoto, *J. Phys. Chem. B* 105 (2001) 1984.
- [23] A.M. More, J.L. Gunjekar, C.D. Lokhande, R.S. Mane, S. H. Han, *Micron* 38(2007) 500.
- [24] O. Bockman, T. Ostvold, G.A. Voyiatzis, G.N. Papatheodorou, *Hydrometallurgy* 55 (2000) 93.