

Growth and characterization of Mn₂O₃ nano thin films by spin coating technique

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Abstract

Mn₂O₃ nano thin films were prepared on glass substrates using spin coating technique by taking manganese acetate (Mn(CH₃COO)₂·4H₂O) as starting material for different molar solutions. Solution was prepared by dissolving Mn(CH₃COO)₂·4H₂O as precursor and mono ethanolamine (MEA) as stabiliser agent and 2-methoxyethanol as solvent. The mixture was stirred at 80°C until to get high viscous transparent solution. A small portion was taken and dropped on to corning glass substrate which was rotated at (3000) rpm for (30) sec and dried at 300°C. The process was repeated for three times to get desired thickness of the film. Prepared films were characterized by using XRD, SEM, UV-Vis spectrophotometer .

Keywords: Thin film, spin coating, XRD, SEM.

أنماء ومعرفة خواص الأغشية النانوية الرقيقة لمادة اوكسيد المنغنيز Mn_2O_3 باستخدام

تقنية تدوير الطلاء $Spin coating$

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الخلاصة

تم تحضير أغشية رقيقة من مادة Mn_2O_3 النانوية على ركيزة من الزجاج باستخدام تقنية ($spin coating$) بأخذ مادة منغنيز $MN (CN_3COO)_2$ كمادة ابتداء للمحاليل المختلفة، تم تحضير المحلول بإذابة $MN (CN_3COO)_2$ كسلائق ومونوا بنانولامين كعامل استقرار و ($Methoxythanol$) كمذيب هذا الخليط خفق عند درجة ($80c$) حتى الحصول على محلول عالي اللزوجة ثم وضع جزء صغير من المحلول على زاوية ركيزة زجاجية دورت بمقدار ($3000 rpm$) دورة بالدقيقة لمدة ($30sec$) ثم خفقت عند درجة ($300c$) وكررت العملية ثلاث مرات للحصول على السمك المطلوب كذلك الغشاء المحضر تم فحصه باستخدام XRD_SEM_UV-VIS .

1. Introduction:

Nanostructured thin films are on stage an important role in the development of nano martial devices. Many researchers have been extending their research to develop thin films and study their properties to discover their applications in different fields. To prepare any commercial device for such applications, it is necessary to develop low cost material by economical method. In this view manganese oxide is a promising functional oxide material due to its low cost and ecofriendly nature. Manganese oxides have received increasing attention due to their unique fundamental properties and potential applications in the field of lithium ion batteries [1], super capacitors [2], anti-bacterial [3], humidity sensors [4], water oxidation [5] and catalysts [6].

There are so many physical and chemical techniques available to grow Mn_2O_3 thin films such as electron beam evaporation [7], electro deposition [8], sputtering [9], Pulsed laser deposition [10], spin coating [11], spray pyrolysis [2] and SILAR [3]. Out of these, spin coating technique is one of the preferred techniques due to its low cost and ease of preparation of device quality thin films.

Molar volume of the solution in the preparation of Mn_2O_3 thin films by spin coating technique [4] plays an important role. The present study illustrates the effect of molar volume of the solution on the structural, morphological and optical properties of the Mn_2O_3 thin films prepared by spin coating technique[4].

2. Experimental:

a) Preparation of Mn_2O_3 thin films:

Manganese acetate (Sigma-Aldrich) was used as the starting material to prepare Mn_2O_3 thin films by spin coating technique. Thin films of Mn_2O_3 were deposited on well cleaned corning glass substrates for different molar solutions. The solution for deposition was prepared by dissolving $Mn(CH_3COO)_2 \cdot 4H_2O$ precursor in 2-methoxyethanol solvent by the use of monoethanolamine[2] (MEA) as stabilizing agent. The mixture was stirred at $80^\circ C$ until to get high viscous transparent solution of 0.2 M, 0.4M and 0.8 M (%), a small portion of this solution has been dropped on to corning glass substrate which was rotated at 3000rpm for 30s and dried at $300^\circ C$. The process was repeated for three times to get desired thickness of the film.

The structural properties of different molar volume (0.2M, 0.4M and 0.8M) Mn_2O_3 thin films were characterized by employing Philips Xpert Pro X-ray diffraction instrument using $CuK\alpha$ ($\lambda=1.54 \text{ \AA}$) in the 2θ range from $20^\circ C$ to $80^\circ C$. The surface morphology of all the films was obtained from SEM measurements carried out using Carl Zeiss EVO 18 SEM system with an accelerating voltage of

20 kV. The optical properties of Mn₂O₃ thin films were determined by using UV-Vis spectrophotometer at room temperature in the wavelength range 200-900 nm.

b) Structural and Morphological characterization

XRD of the samples was carried out using CuK_α radiation [1] on a STOE high resolution X-ray powder diffractometer with parallel beam optics set to θ–2θ geometry. For all the measurements, the angle of incidence of the X-rays was kept at 0.5° and diffraction space was scanned over a 2θ range of 15–80°. to investigate the structural and crystallographic phases present in the films using nickel-filtered CuK_α radiation (λ= 0.15418 nm) a voltage of 40 kV and a current of 30 mA was applied. The average size of Crystallites (D) of In₂O₃ films was estimated using Debye Sherrer formula.

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

Where D-crystallite size, λ-wavelength of CuK_α radiation (0.15418nm), k- Constant (0.9), β-FWHM, θ- Bragg's diffraction angle.

The microstrain (ε) is calculated using the relation:

$$\epsilon = \frac{\beta \cos\theta}{4} \text{ ----- (2)}$$

The dislocation density (δ) is calculated by using the formula:

$$\delta = \frac{1}{D^2} \text{ ----- (3)}$$

Where D is crystallite size.

3. Results and Discussion:

Structural studies:

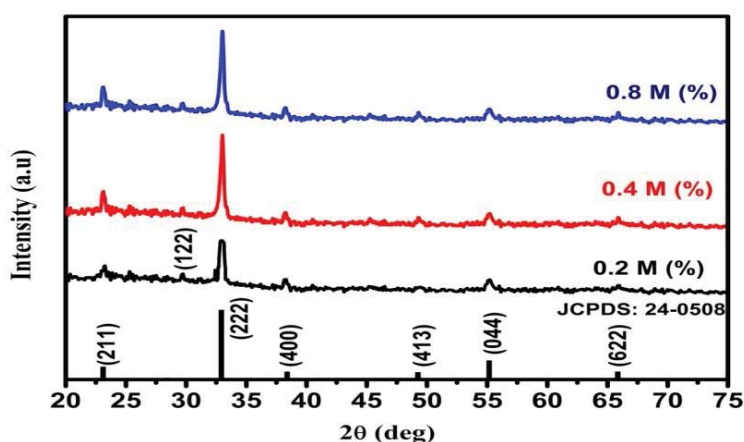


Figure. 1. XRD pattern of Mn₂O₃ thin films for different molar volum

Figure.1. shows the X-ray diffraction patterns of spin coated Mn_2O_3 thin films for different molar volumes. From the figure it is clear that all the films are polycrystalline in nature with cubic structure (JCPDS card no: 24 -0508). 23.10, 28.42, 32.92, 38.39, 49.25, 55.177, 65.85 (211), (122), (222), (400), (413), (044), (622). ; Lattice constants $a=9.45 \text{ \AA}$, $b=9.42 \text{ \AA}$, $c=9.4 \text{ \AA}$ Orthorhombic structure. The preferred orientation of all the films is in (2 2 2) direction, the intensity of this peak is increasing with molar volume. Figure.2. shows variation of crystallite parameters with varying precursor molarity from this crystallite size increases with increasing molar volume of the solution correspondingly lattice strain, dislocation density and number of crystallites for unit volume also decrease.

Morphological studies:

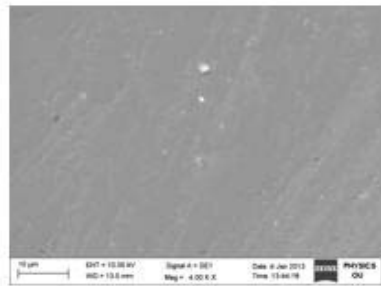


Figure.3(a).

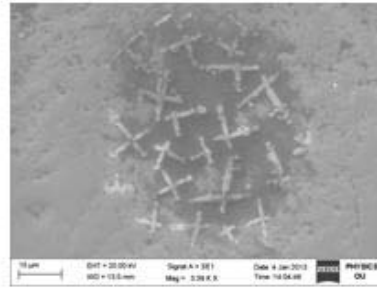


Figure.3(b).



Figure.3(b)(Magnified).

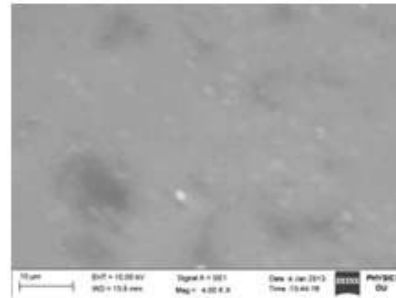


Figure.3(c).

Figure.3. (a)(b) and (c) SEM micrographs of Mn_2O_3 thin films for different molar volumes.

Figure 3.(a)(b) and (c). Displays the surface SEM images of the spin coated Mn_2O_3 thin films for different molar volumes. It can be seen from the SEM images that the morphology of the samples is different for different molar volumes, but all the sample films are very uniform, crack free and

compact. SEM micrograph of 0.4M (%) solution was shown nano junction like morphology and it shown magnified in Figure.(b)(magnified).

Optical studies:

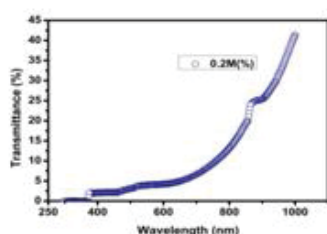


Figure.4(a)

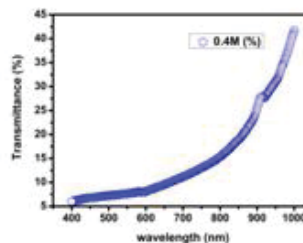


Figure.4(b)

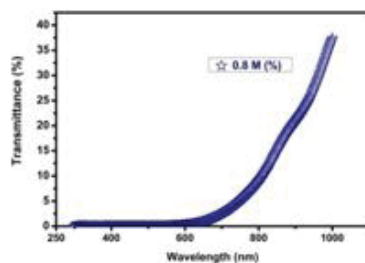


Figure.4(c)

Figure .4.(a)(b) and (c) Optical transmittance spectra of Mn_2O_3 thin films for different molar volumes.

Optical studies of Mn_2O_3 thin films for different molar volumes were performed by UV-Vis spectrophotometer. Figure.4.(a)(b) and (c) shows the optical transmittance spectra of Mn_2O_3 thin films for different molar volumes. Optical transmittance of these Mn_2O_3 thin films decreases towards lower wavelengths and transmittance edge shifted towards higher wavelengths.

4. Summary:

In summary, the influence of molar volume on the structural, optical and morphological properties of spin coated Mn_2O_3 thin films was investigated. Mn_2O_3 thin films of different molar volumes (0.2M, 0.4M and 0.8M) have been deposited on corning glass substrates and subjected to their structural, morphological and optical characterization through XRD, SEM and UV-Vis spectrophotometer studies respectively. From the XRD results it is clear that all the films are polycrystalline in nature with cubic structure and the preferred orientation of all the films is in (2 2 2)

direction. From the SEM images it is seen that all the sample films are uniform, crack free and compact. The results of optical studies suggest that the optical transmittance was found to vary with varying molar volumes of Mn_2O_3 thin films.

5- conclusion:

From the XRD results it is clear that all the films are polycrystalline in nature with cubic structure and the preferred orientation of all the films is in (222) direction. From the SEM images it is seen that all the sample films are uniform, crack free and compact. The results of optical studies suggest that the optical transmittance was found to vary with varying molar volumes of Mn_2O_3 thin films.

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