Effects of Thickness on the Structural and Optical Properties of Mn3O4 Nanostructure Thin Films

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Abstract. In this work, nanostructured Mn3O4 thin films at different of thickness (200, 250, 300, 350) nm were deposited on substrate made from glass by chemical spray pyrolysis technique with substrate temperature at 400 °C. However, during this process, The structural and optical properties of these films have been investigated using XRD, and UV-Visible spectroscopy. The X-ray Diffraction (XRD) results showed that all films are polycrystalline in nature with tetragonal structure and preferred orientation along (211) plane. The crystallite size is determined by Scherer’s formula and W-H analyses and it is found that it decreases as the thickness increasing. The optical energy gap for allowed direct electronic transition was calculated using Tauc equation. It was found that the band gap decreases when the thickness increasing. The variables of the optical properties containing (coefficient of absorption, parts of real and imaginary for dielectric constant) and estimated as a function of the photon energy. Coefficient extinction of thin film was valued as a wavelength function.

Keywords: Structural Properties, Optical Properties, Mn3O4 thin film.

1. Introduction

Manganese oxide thin films is metal oxide semiconductors and used for UV detectors. As chief grouped of (II—IV) semiconductors film with versatile characters, the films have been several application in many field: e.g., catalysis’s, transducers, battery, sensors for gas and super capacitors [1]. Manganese oxides is one among of the transition metal oxides, manganese oxides are very attractive anode material for lithium-ion batteries due to the high abundance of Mn, low of cost, and environmental benignity. Manganese oxides have several phases of crystalline [(MnO), (Mn3O4), (Mn2O3), and (MnO2)] which have unlike structural and compositional properties [2]. Several methods is developed to create of manganese oxides, such as electrochemical deposition, sol – gel technique, , electrochemical method,
chemical bath method, electrostatic spray deposition, APCVD and hydrothermal synthesis [3] Spray pyrolysis was one of the most cost effective techniques to prepared manganese oxides films due to its ability to deposit great uniform area, low of price, simplicity and little temperature of deposition [3,4]. In this research we deposited Mn3O4 thin film on substrate made from glass by a chemical spray method, and calculated the structure and optical properties of these films with the aim of understanding properties of physical of the obtained Mn3O4 thin film.

2. Experimental Procedures

Chemical spray pyrolysis technique was used to deposit Mn3O4 thin films with different thickness on glass substrates at temperature of (400 ºC). The spraying of solution were prepared by dissolving appropriate quantity of manganese acetate anhydrous Mn(CH3COO)2 in distilled water at room temperature by used magnetic stirrer of(30) minute and resulting of solution were spraying on substrate temperature at 400 ºC. The thickness of the prepared films have different thickness (200, 250, 300 and 350) nm where measured by gravimetric method. Other conditions such as distance of spray nozzle substrate (28) cm, time of spray (10 s), interval of spray (120 s) and the transporter gas of (1.6) bar pressure was keeps constant with all test samples. The study of structure characterized used X-rays Diffraction, and the UV–VIS transmission spectra for the prepared film Mn3O4 was recording about (300–900) nm by Spectrophotometer (Type: UV-Visible1800) at room temperature.

3. Results

3.1. XRD analysis

Figure (1) shows XRD patterns of, nanostructured Mn3O4 thin films with changed thickness. Its seen that totally the patterns display of diffraction peaks about (2θ ~ 32.4°, 35.9° and 44.4°) referred to (103), (211) and (220) preferred direction respectively and agreement with number card 24-0734 of the Joint Committee of Powder Diffraction Standards (ICDD). The high peak happens at 2θ ~35.9° has (211) plane. The locations of these peaks were founded of other diffraction peaks due to the conclusion that is films which was polycrystalline with a tetragonal structure, and agreement with [2, 5]. The strength of crests increases as the ratio thickness rises. One can observed also that there is a small shift of (2θ) location of Mn3O4 thin films. This change may ascent from the strain induced once the additives are combined into the crystal lattice [5, 6].

![Figure 1. X-ray pattern of (Mn3O4) films at various thickness.](image-url)
The mean of crystallite size ($D_{av}$), were evaluated by Scherer’s formula [6-10]:

$$D_{av} = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where: $\lambda$ = wavelength(1.5406 Å for Cu Kα), $K$ = 0.9 of $\beta$ : the full width of half maximum of peaks (in radians) and $\theta$ : Bragg's diffraction angles of XRD peaks. It's seen that the mean of crystallite size of Mn$_3$O$_4$ film in nanostructure range and decreases as thickness increasing. The bigger crystallite size values showed well crystallization for the film [6, 7].

| Sample | 2 $\theta$ deg | $d_{ab}$ Å | hkl | FWHM $\beta$ deg |
|--------|----------------|------------|-----|-----------------|
| 1      | 32.49          | 2.7536     | (103) | 0.38            |
|        | 35.8           | 2.5062     | (211) | 0.16            |
|        | 43.62          | 2.0733     | (220) | 0.3             |
|        | 32.63          | 2.7421     | (103) | 0.23            |
| 2      | 36.14          | 2.4834     | (211) | 0.36            |
|        | 44.62          | 2.0291     | (220) | 0.24            |
|        | 32.42          | 2.7594     | (103) | 0.6             |
| 3      | 35.94          | 2.4968     | (211) | 0.78            |
|        | 44.54          | 2.0326     | (220) | 0.3             |
|        | 32.27          | 2.7718     | (103) | 0.34            |
| 5      | 36             | 2.4927     | (211) | 0.86            |
|        | 44.37          | 2.0400     | (220) | 0.54            |

The average of crystallite size also can be calculated by W - H formula [8, 11]

$$\beta \cos \theta = \frac{k\lambda}{D_{av}} 4\varepsilon \sin \theta$$  \hspace{1cm} (2)

Where: $S$ is the microstrain in the sample. A plot are drawn (4 sin $\theta$) of x-axis and of y-axis ($\beta \cos \theta$) for Mn$_3$O$_4$ thin films as displayed of figure (2). As of the linear fit of the data, the crystallite size were calculated from the y-intercept, and slope of the fit are represented $S$. The micro strains were induced during the formation nanomaterial, and will be raising as of stretching or compression of lattices. The micro strain was produced by changing displacements of atom with respect to their reference lattice places [9, 12]. From these effects, it's seen that the micro strain is increases while the crystallite size decreased when thickness increasing. Table 2 are summarize of results obtained from W - H analysis, these results is agreement with the results of Scherer’s way. The micro strain value are negative which shows the occurrence of compression of lattice, as displayed of table 2.
The dislocation density (δ) can be calculated as the following [8, 13, 14]:

\[
\delta = \frac{1}{D_{av}^2}
\]  (3)

there is inverse relation between dislocation density and crystallite size so that dislocation density increased when the values of crystallite size decreasing, and when the dislocation density decreases, strong microstrain is not induced with the grain. 

The number of crystallites \((N_o)\) can be estimated by [8, 13] :

\[
N_o = \frac{t}{D_{av}^3}
\]  (4)

Where \(t\) : is thickness. It can be observed that the number of crystallites for composites films increases with increased of thickness due to the increase in the values of crystallite size.

The “Texture coefficient” \(T_c\) can be valued by [6, 14]:

\[
T_c(h,k,l) = \frac{I(h,k,l)/I_o(h,k,l)}{N^{-1}\sum I(h,k,l)/I_o(h,k,l)}
\]  (5)

Where: \((I(h,k,l))\) : the measured intensity, \((I_o(h,k,l))\) take from ICDD data, \(N\) = reflection number and \(hkl\) is Miller indices. The \((T_c)\) are used to describing to preferred orientation \((hkl)\) for the growth on the crystal in a polycrystalline films as displayed on the table2, its seen that the \((T_c)\) values were smaller than one this indicate the lack of grains oriented in that direction. As \(T_c(hkl)\) increasing, the preferential of the crystallites growth in the direction are perpendicular to \(hkl\) planes was the greater [15]
Table 2. Structural parameters and comparison between Scherrer and W-H methods of Mn$_3$O$_4$ thin films

| Sample | 200nm | 250nm | 300nm | 350nm |
|--------|------|------|------|------|
| DD$_{av}$ (nm) | Scherrer | 34.2 | 31.7 | 17.7 | 16.8 |
| W-H | 34.7 | 28.8 | 8 | 5.2 |
| $\delta$(line. cm$^{-2}$)*10$^{-18}$ | Scherrer | 8.54 | 9.95 | 31.9 | 35.4 |
| W-H | 8.3 | 12 | 156 | 370 |
| $N_o$ (cm$^{-2}$)*10$^{-18}$ | Scherrer | 49.9 | 78.4 | 541 | 738 |
| W-H | 47.8 | 104 | 5859 | 25000 |
| Microstrain (S) | -0.074 | -0.107 | -0.552 | -0.925 |
| Tc | 0.5 | 0.53 | 0.54 | 0.6 |

3.2. Optical investigation

Optical absorption spectra of all samples student in range of spectral 300 to 900 nm when recording by used UV–Vis spectrophotometer. The analysis are dependence of absorption coefficient on photon energy in the high absorption regions is performed to obtain the detailed information around the energy gap of samples[10]. Figure 3 show the relative between transmittance and wavelengths of Mn$_3$O$_4$ film at different thickness. It’s clear that transmittance of all films increasing as increased of wavelength of (300 - 550) nm, and then increasing little by little at high wave length. Its observed that of transmittance for Mn$_3$O$_4$ thin films decreases as thickness increasing. The decreases in transmittance films can be attributed to the increased of the lattice defects and homogeneity of suspension and hence the increasing of absorption.

![Figure 3. Transmittance for Mn$_3$O$_4$ films at various thickness.](image-url)
The absorption coefficient is evaluated by used [2, 7, 10]:

$$\alpha = \frac{2.303A}{t} \quad (6)$$

Where: A is absorbance, t is the thickness and \( \alpha \) is the coefficient of absorption. It's seen that all films need greater absorption coefficients of visible series of spectra, as seen in figure 4. The coefficient of absorption increasing when energy photon \((h\nu)\) increased. The absorption coefficient of \( \text{Mn}_3\text{O}_4 \) film at changed thickness have values of \((\alpha > 10^4) \) 1/cm which are implies the increasing on probabilities of the amount of direct transitions and observed that the coefficient of absorption for \( \text{Mn}_3\text{O}_4 \) thin films decreases as thickness increasing.

![Figure 4. Relative between coefficient of absorption (\( \alpha \)) and energy photon for \( \text{Mn}_3\text{O}_4 \) films at various thickness.](image)

The optical energy gap \((E_g)\) estimated by [1, 6, 10]:

$$ah\nu = B(h\nu - E_g)^r \quad (7)$$

Where: \( \alpha \) = absorption coefficient, \( h\nu \) = photon energy, \( B \) : constant is not depend of photon energy and \( r \) have four several values (1/2) for to allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions. graph between \((ah\nu)^2\) and \((h\nu)\) in eV. The values of the band gap certain by straight line to \((ah\nu)^2 = 0\), as shown in Figure 5. Its seen that the value of band gap is decreasing as thickness increased, this decreasing of gap can be relating to the structural change of film with high thickness and the greater crystallite size value indicate well crystallization of the film and provide a large surface area that could increase the probability of surface trapping, which is highly transition of electrons to the surface reaction[6, 7, 15]
The extinction coefficient ($K_o$) was calculated using relation [10]:

$$K_o = \frac{\alpha \lambda}{4 \pi}$$  \hspace{1cm} (8)

Where: $K_o$ is the extinction coefficient and $\lambda$ is the wavelength of incident photon. The figure 6. shown the relative between of the coefficient of extinction and wavelengths of Mn$_3$O$_4$ film at changed of thickness. Its seen that the extinction coefficient ($K_o$) decreasing at little wave lengths (320-550) nm and next that values for ($K_o$) are remains constant. The growth and drop in value of ($K_o$) is connected straight for the light absorption. The lesser values for ($K_o$) of wave length about (550– 900 nm) implies that the film absorbed light of this area is very simply.

### Table 3. Energy gap of Mn$_3$O$_4$ thin films at different thickness

| Sample | (200) nm | (250) nm | (300) nm | (350) nm |
|--------|----------|----------|----------|----------|
| $E_g$ (eV) | 3.83  | 3.51  | 3.47   | 2.85    |

Figure 5. Variation of $(\alpha h\nu)^2$ with $(h\nu)$ of Mn$_3$O$_4$ films at various thicknesses.
The dielectric constant estimated by [16,17]:
\[
\varepsilon = \varepsilon_1 - i\varepsilon_2
\]  
(9)
Where: \( \varepsilon_1 \) : real part and \( \varepsilon_2 \) : imaginary part of dielectric constant. For estimated the dielectric constant in two parts are used the expressions[16]:
\[
\varepsilon_1 = n^2 - K_0^2
\]  
(10)
\[
\varepsilon_{12} = 2 n K_0
\]  
(11)
Where \( n \) is refractive index. Figure (7) shown the relative between real and imaginary part for dielectrics constant and energy of photon to the Mn\(_3\)O\(_4\) film at various thickness. It's seen that these real part and imaginary is increasing as increased of photon energy. It's noticed that the real and part imaginary are decreased when thickness increasing.

**Figure 6.** Relative between coefficient of the extinction and wavelengths for Mn\(_3\)O\(_4\) film at various thickness

**Figure 7.** Real \((\varepsilon_1)\) and imaginary \((\varepsilon_2)\) parts of dielectric constant vs. photon energy for Mn\(_3\)O\(_4\) films at various thickness
4. Conclusion
In this study, Nanostructured Mn$_3$O$_4$ thin films at various thickness were successfully deposited on glass substrates at (400 °C) by chemical spray pyrolysis technique using. XRD patterns of the Mn$_3$O$_4$ thin films indicate that all films are polycrystalline with tetragonal crystalline structure. The microstrain in the films is induced during the growth of thin films by varying displacements of the atoms with respect to their reference lattice position. All values of microstrain were negative which indicates the occurrence of compression in the lattice. the crystallite size decreases with increasing of thickness. The band gap decreases when the thickness increases.

5. References
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