The Effect of Annealing on the Structural and Optical Properties of Mn$_2$O$_3$ Thin Film Prepared by Chemical Spray Pyrolysis

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Abstract: *Thin films of Mn$_2$O$_3$ are synthesized using a simple chemical spray pyrolysis method on substrate from glass and then annealed in 400°C for one hour in air. By using the X-ray diffraction we characterize the structure properties of the deposited films. The results indicate that the films are polycrystalline with cubic structure and strong (222) preferred orientation. Atomic force microscope (AFM) was used to study Morphological properties of the samples. By Using UV-VIS spectrometer the energy band gap and optical constants were calculated.*

**Keywords:** chemical spray pyrolysis, Mn$_2$O$_3$, Structural and Optical Properties

1. Introduction

Manganese Oxide was a transition metal oxide. Cubic (Mn$_2$O$_3$), tetragonal Mn$_3$O$_4$ and cubic MnO structures. Among these oxide, Dimanganese trioxideMn$_2$O$_3$ is most stable. Manganese oxide Thin films can be applied as rechargeable batteries, catalysts, electrochemical capacitors, sensors and magneto electronic devices.[1] Different structural, electronic, and magnetic properties of manganese oxides are fundamentally influenced by several oxidation conditions and locations of the manganese ions in the unit cell of these oxides. Various process employed to produce manganese oxide films, such as sputtering, electron beam evaporation, pulse laser deposition molecular beam epitaxy, electrochemical, spray pyrolysis, and sol – gell[2,3]. The spray pyrolysis technology has the merit of low cost, easy to use, safe and appropriate for scientific studies. Some papers notify on the output of manganese oxide thin films by spray pyrolysis and their optical and electrical properties. The optical properties of Mn$_2$O$_3$, Mn$_3$O$_4$ and MnO were calculated and it was establish that the not filled orbit of the transition oxides thin films have optical energy band gaps in the visible region .Mn$_2$O$_3$ has comparatively high Conductivity, p-type semiconductor, thermodynamic stability[4,5].

2. Experimental

Mn$_2$O$_3$ thin films were prepared by chemical spray pyrolysis technique. We use the aqueous solution consist of 0.1M of manganese acetate tetra hydrate (Mn(C$_2$H$_3$O$_2$)$_2$-4H$_2$O) as a precursor salt, and 50mL from deionized water as a solvent, homogeneous mixture was accomplished by employing magnetic stirrer. Ultrasonically (Model SB-200 DTDN) glass slides were cleaned then putted on a solid uniform thermal conductor surface to supply convenient heating with consistency to films. A heater was applied as heat source to supply temperature of around 250°C. The typical conditions were the following parameters, spray time (15 sec), average deposition (10 cm$^3$/min), distance between nozzle and substrate (30 ±1cm). Thicknesses of the patterns were evaluated using the weighting technique and the thicknesses of the prepared films were (600±20)nm. The prepared films was then annealed at 400°C for 1 h and allowed to cool for room temperature. To study the structural properties of the prepared samples we use X-ray diffraction type Philips with the following specifications: target CU, wavelength: 1.5406Å, the optical measurements comprise measuring the absorbance and transmittance with range from (300-900) nm by using UV- VIS spectrophotometer type Jenway 6800.

<table>
<thead>
<tr>
<th>Sample</th>
<th>hkl</th>
<th>2θ(deg)</th>
<th>d Å$^3$</th>
<th>FWHM(deg)</th>
<th>Gnm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$O$_3$ before annealing</td>
<td>222</td>
<td>33.0565</td>
<td>2.7076</td>
<td>0.3425</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>36.0245</td>
<td>2.4911</td>
<td>0.3250</td>
<td></td>
</tr>
<tr>
<td>Mn$_3$O$_4$ after annealing</td>
<td>222</td>
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<td>2.7075</td>
<td>0.3031</td>
<td>27.4</td>
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<tr>
<td></td>
<td>321</td>
<td>35.4753</td>
<td>2.5284</td>
<td>0.1356</td>
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</tbody>
</table>

3. Results and Discussion

3.1 Structural and morphological properties

Fig. 1. showed the X-ray diffraction of Mn$_2$O$_3$ films before and after annealing, all the peaks are sharp it is evident that the films deposited are polycrystalline in nature and the positions of X-ray diffraction peaks fit well with the cubic structure with preferred orientation (222) corresponding to ASTM cards no: 41-1442. The peaks exhibit small increasing in the intensity with increasing temperature. The average grain size of Mn$_2$O$_3$ thin film samples were calculated by employing the Scherrers's equation,[6].

$$D=0.94\lambda/\beta \cos \theta \quad \ldots \ldots (1)$$

The crystallite size of the films prepared was shown in Table 1.
have a high optical absorbance in the visible region, which decreases gradually as the wavelength increases, we can notice the absorbance increases for annealed film and shifted to longer wavelengths. This may be attributed to the creation of levels at the energy band by increasing temperature and this leads to the shift of peak to smaller energies.

The optical energy band gap $E_g$ of the assembled thin films was calculated, by using the following equation [7].

$$\alpha h\nu = A (h\nu - E_g)^n$$  \hspace{1cm} (2)

Where $A$ is constant, $h\nu$ is the incident photon energy, and $n$ is a factor whose value dependent on the nature of band transition, $n = 1/2$ or $3/2$ for direct allowed and direct forbidden transition. The values of direct optical band gap was found to be 2.8 Ev for Mn$_2$O$_3$ before annealing and 2.4 Ev after annealing, and the indirect optical band gap was found to be 2.4 Ev for Mn$_2$O$_3$ film before annealing and 2.2 Ev for annealed Mn$_2$O$_3$ film which is in agreement with the report[8], which is shown in Fig.(4). The annealing procedure enhance crystallinity and increases average grain size that result is decreasing defects, therefore band gap energy decreased. The extinction coefficient ($k$) has been premeditated using the following relation[9]and showed in Fig.(5).

$$k = \frac{\alpha \lambda}{4\pi}$$ \hspace{1cm} (3)

3.2 Optical properties

We study The optical absorption spectrum of the prepared films in the range of (300- 900 nm) before and after annealing shown in Fig.(3). It is obvious that Both the films
We can perceive from Fig.(5) that the extinction coefficient, generally, decreases with the increase of wavelength for all films. Also its value increases by annealing operation. This is ascribing to the same reason introduced earlier in the absorption spectrum. Also we studied the spectrum of the refractive index as be seen in Fig.(6). It can be perceive that the refractive index increases with annealing this is imput to the increase in the absorbance and decreases in the transmittance. The difference of the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant values facing wavelength before and after annealing are be in view in Fig.(7). The $\varepsilon_r$ values were computed using the formulas\cite{10}

$$\varepsilon_r = \frac{n^2 - k^2}{n^2 + k^2} \quad \text{........... (4)}$$

$$\varepsilon_i = \frac{2nk}{n^2 + k^2} \quad \text{........... (5)}$$

The $\varepsilon_r$ values are higher than that of $\varepsilon_i$ values. It is seen that the $\varepsilon_r$ and $\varepsilon_i$ values decrease with annealing.

4. Conclusion

Thin films of Dimanganese trioxide Mn$_2$O$_3$ with thicknesses of (600±20)nm were arranged by chemical spray pyrolysis method and annealed for one hour with 400°C. The XRD results showed that all films are polycrystalline in nature with a cubic structure and the preferred orientation was along the (222) plane for all films. The absorbance for all prepared films increases as the wavelength increases and the band gap decreases with increasing temperature.

References


