The Effect of Annealing on the Structural and Optical Properties of Mn_2O_3 Thin Film Prepared by Chemical Spray Pyrolysis

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Abstract: ***Thin films of $Mn_2O_3$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 wecharacterize the Structure properties of the deposited films, The results indicate that the films are polycrystalline with cubic structure with a 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_2O_3, Structural and Optical Properties

1. Introduction

Manganese Oxide was a transition metal oxide. Cubic (Mn_2O_3), tetragonal Mn_3O_4 and cubic MnO structures . Among these oxide, Dimanganese trioxide$Mn_2O_3$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_2O_3,Mn_3O_4 and MnO were calculated and it was establish that the not filled orbits of the transition oxides thin films have optical energy band gaps in the visible region ,Mn_2O_3 has comparatively high Conductivity, p- type semiconductor, thermodynamic stability[4,5].

2. Experimental

Mn_2O_3 thin films were prepared by chemical spray pyrolysis technique .we use the aqueous solution consist of 0.1M of manganese acetate tetra hydrate ($Mn(C_2H_3O_2)_2$,$4H_2O$)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: 1.5406A°.the optical measurements comprise measuring the absorbance and transmittance with range from (300-900) by using UV- VIS spectrophotometer type Jenway 6800.

Sample	hkl	2θ(deg)	d(A°)	FWHM(deg)	G(nm
Mn_2O_3 before annealing	222	33.0565	2.7076	0.3425	24.2
	321	36.0245	2.4911	0.3250	
Mn_2O_3after annealing	222	33.0580	2.7075	0.3031	27.4
	321	35.4753	2.5284	0.1356	

3. Results and Discussion

3.1. Structural and morphological properties

Fig. 1showed the X-ray diffraction ofMn_2O_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 toASTM cards no:41-1442.The peaks exhibit small increasing in the intensity with increasing temperature . The average grain size of Mn_2O_3 thin film samples were calculated by employing the Scherrer's equation,[6].

$$D=0.94\lambda/\beta \cos\theta \quad \text{..........(1)}$$

The crystallite size of the films prepared was shown in Table1.

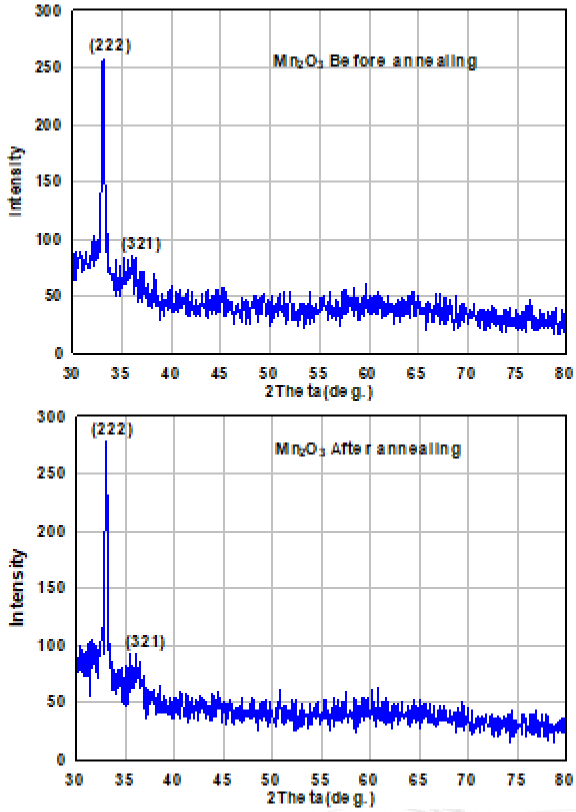
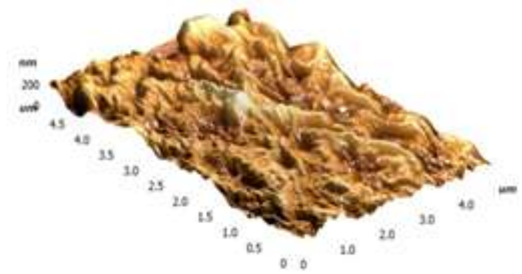


Figure 1: XRD patterns of thin films

Fig.2 display 3-D images AFM of Mn_2O_3 thin films before and after annealing. The growthin average diameter grain due to increase in annealing temperature is clearly seen from the AFM image. The average diameter of grain of the composed films was found to be in the range of(204-219)nm

A



B

Figure 2: 3D AFM images of deposited thin film, A before annealing, B after annealing

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 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.

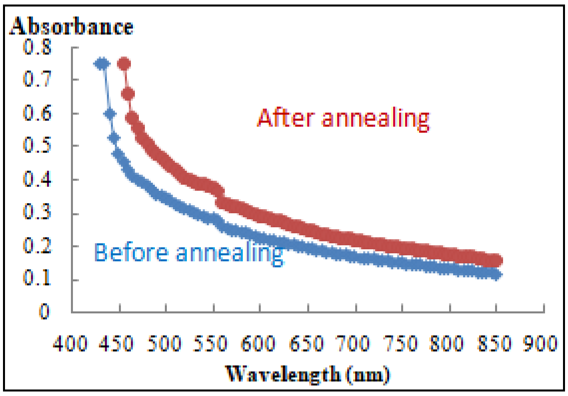


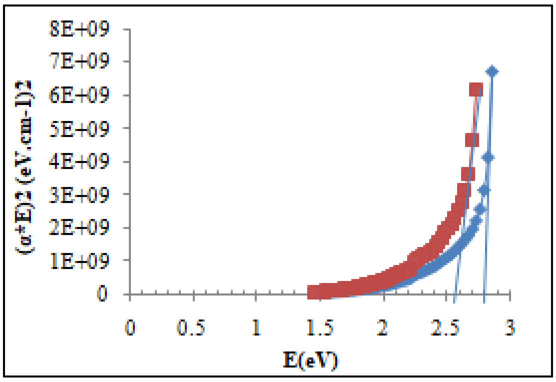
Figure 3: Absorption spectrum forMn_2O_3 thin films

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

$$\alpha h\upsilon = A(h\upsilon - Eg)^{n} \text{ --------------------(2)}$$

Where A is constant, hυ 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 forMn_2O_3 before annealing and 2.4 Ev after annealing, and the indirect optical band gap was found to be 2.4 Evfor Mn_2O_3 film before annealing and 2.2 Ev for annealed Mn_2O_3 film which is in agreement with the report[8], which is shown in Fig.(4).theannealing 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).

$$k = \frac{\alpha\lambda}{4\pi} \text{.............(3)}$$



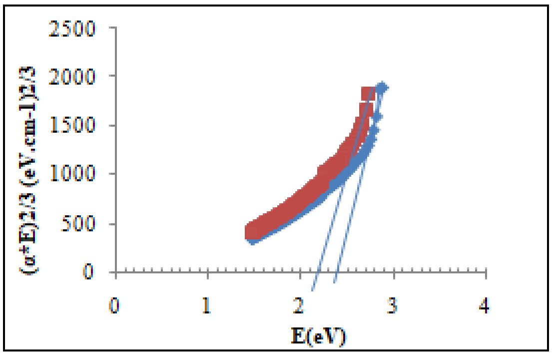


Figure 4: The direct and indirect optical energy band gap for Mn_2O_3 films

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 impute to to the increase in the absorbance and decreases in the transmittance. The difference of the real (εr) and imaginary (εi) parts of the dielectric constant values facing wavelength before and after annealing are be in view in Fig.(7). The εrand εi values were computed using the formulas[10]

$$\varepsilon r = no^2 - k^2 \quad \ldots\ldots\ldots\ldots (4)$$

$$\varepsilon i = 2no\, k \quad \ldots\ldots\ldots\ldots.. (5)$$

The εr values are higher than that of εi values. It is seen that the εr and εi values decrease with annealing

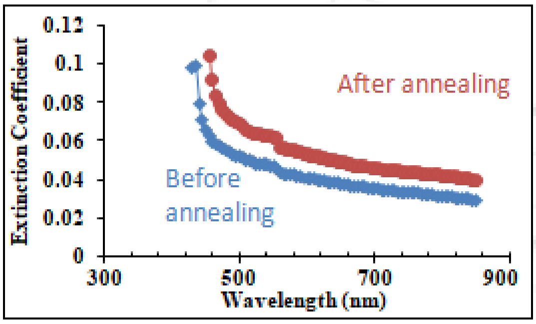


Figure 5: Extinction coefficient spectrum for Mn_2O_3thin films

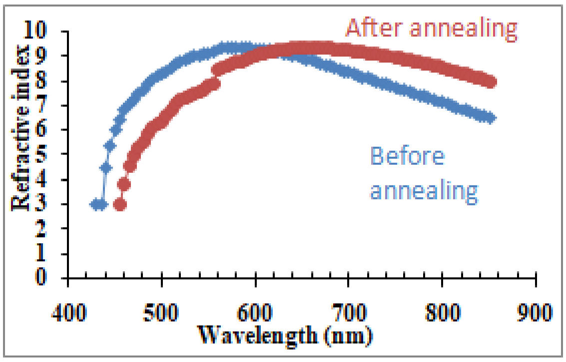


Figure 6: Refractive index as spectrum forMn_2O_3films

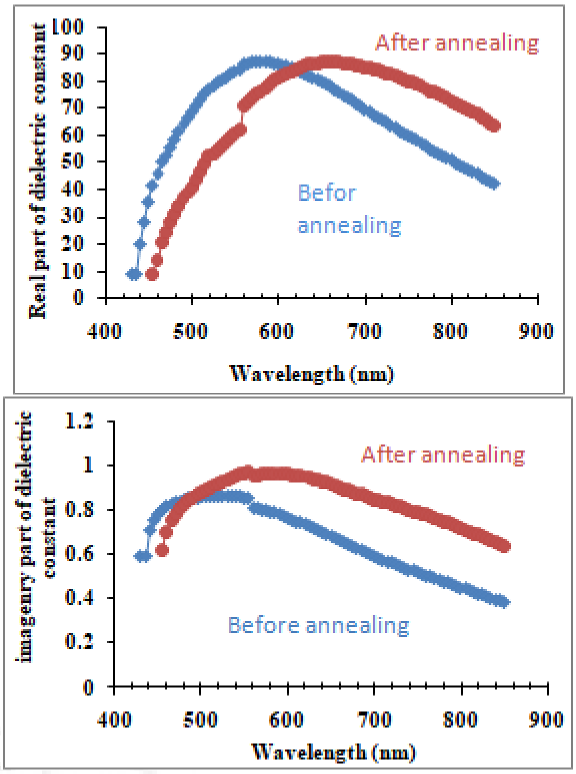


Figure 7: difference of real and imagenary part of dielectric constants a function of wavelength for Mn_2O_3 films

4. Conclusion

Thin films of Dimanganese trioxide Mn_2O_3 with thicknesses of (600±20)nmwere arranged by chemical spray pyrolysis method and annealed for one hours with400°C.The. 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. Theabsorbance for all prepared films increases as the wavelength increases and The band gap decreases with increasing temperature

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