IOSR Journal of Engineering (IOSRJEN)
e-ISSN: 2250-3021, **p**-ISSN: 2278-8719
Vol. 3, Issue 4 (April. 2013), ||V4 || PP 52-57

Structural and Optical Properties of MnO_2: Pb Nanocrystalline Thin Films Deposited By Chemical Spray Pyrolysis

Ahmad H. Al-Falahi
Physics Department, College Of Education for Pure Sciences Anbar University, Iraq

Abstract: MnO_2 thin films were deposited by chemical spray pyrolysis method on glass substrates and then doped by pb:3% and 5%. Structural properties of the prepared films were studied by means of x-ray diffraction (XRD), all patterns of the films are polycrystalline. The surface morphology of the films were investigated by using atomic force microscope (AFM) technique. The optical properties were studied by UV-VIS spectrophometer, the absorption coefficient and optical band gap were calculated. Extinction coefficient, refractive index, and the dielectric constant were investigated.

Keywords: *Chemical spray pyrolysis, MnO_2: pb thin films, Structural and optical properties, X-ray diffraction.*

.

I. INTRODUCTION

Thin film technology occupy a prominent place in basic research and the use of thin film semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs. The review of literature shows that thin films technology has been explored by many research groups. This has led to the emergence of several deposition techniques most of which require steady/ uninterrupted power supply because involve high temperature process [1].

In the last decade, synthesis and characterization of manganese oxides in various oxidation states and/ or different structures have been intensified due to their promising potential for application in various fields, such as catalysis, secondary batteries and supercapacitors [2-3].

MnO_2 thin films can be fabricated by: chemical bath deposition (CBD) [4], pulsed laser deposition (PLD) [5],R.F-Sputtering [6] and chemical spray pyrolysis [7].

Usually MnO_2 is a transparent semiconductor with an n-type carrier in conduction [7]. MnO_2 thin films prepared by facile solution method is promising as electrodes for supercapacitors [8].

II. EXPERIMENTAL

In this work MnO_2 thin films were prepared by chemical spray pyrolysis deposited on micro glass slides. Spray solutions were prepared by mixing 0.1 M of $MnCl_2$:$2H_2O$ in $Pb(NO_3)_2$, which were then mixed in a certain amount of solution for each experiment by a magnetic stirrer. Automated spray solution is transferred on the hot substrate kept at the normalized deposition temperature of 250 $^{\circ}$C with the help of carrier gas.

Thickness measurements of the films have been carried out using optical method, thickness was found to be 400 ± 20 nm.

To determine the nature of the growth and structural characteristics of the prepared thin films, an x-ray diffraction (XRD) obtained for diffract meter type Philips PW.1840 with target CU-Kα. A UV- VIS spectrophotometer type Jenway 6800. UV/ VIS wase used to measure the absorbance and transmittance in the wavelength range (200-1100) nm, and from these measurements the optical parameters were calculated.

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Figure. 1 shows the(XRD) spectra of MnO_2**,** MnO_2: 3% pb and MnO_2: 5% pb thin films. All patterns of the prepared films are polycrystalline with preferred orientation (101) which corresponds to orthorhombic structure corresponding to (ASTM) cards. The peaks showed small shifting toward large angles. All phases and planes of MnO_2 and MnO_2: pb are shown in Table 1.

Table.1:XRD patterns of prepared films.

Sample	G.S	2theta	hkl	phase
MnO_2	20nm	22.1	101	orthorhombic
		35.1	301	
MnO_2 3% pb	25nm	22.7	101	orthorhombic
		35.4	301	
Mno_2 5% pb	31nm	22.89	101	orthorhombic
		35.58	301	

The grain size of the synthesized MnO_2 and MnO_2 : pb thin films have been calculated from the full width at half maximum (FWHM) of the diffraction peaks using the Debye-Scherrer formula [9]

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

Where D is the mean grain size, α is a shape factor,λ is the wavelength of x-ray used for the diffraction measurements (here, λ= 1.54056 A°),and β is the FWHM of the diffraction peaks.
The grain size of the prepared films was found to be in the range of(20nm to31nm) as shown in Table 2.

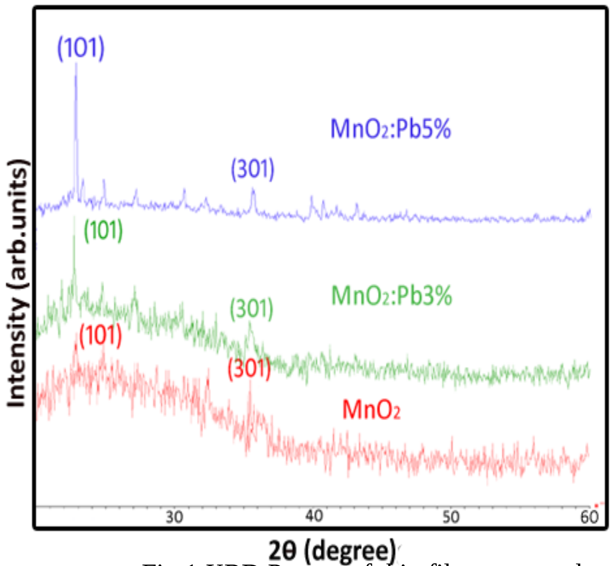


Fig.1:XRD Pattern of thin films prepared.

3.2 Morphology

A typical AFM image of the deposited films is shown in Figure 2. This particular image corresponds to the film deposited on glass substrate shows a good morphology of the prepared films, it is shown from Figure 2 that the film's surface has a good homogeneity which makes the deposited films suitable for applications in photovoltaic devices, also the pb doping caused an increase in the roughness average of the films surface and the average diameter grain size which applies with the results of x-ray diffraction, as shown in table 2.

Table.2:Effect of pb doping on morphology of film surface.

Sample	Roughness avg.	Avg. diameter
MnO_2	0.496 nm	72.65 nm
MnO_2:3%Pb	1.51 nm	85.67 nm
MnO2:5%Pb	3.97 nm	87.18 nm

3.3 Optical Characterization

The optical absorption of the prepared films has been studied in the range of (200- 1100 nm). The variation of optical density with wavelength is analyzed to find out the nature of transition, for different films were used to calculate the absorption coefficient (α) using the relation [10]

$$\alpha = \frac{2.303\,A}{t} \quad \text{---------------- (2)}$$

Where A is the absorbance, and t is the film thickness.

The variation of the absorption coefficient (α) as a function of wavelength (λ) for polycrystalline MnO_2 and MnO_2:Pb thin films is shown in Figure 3. It is clear that the value of α decreases with the increase in wavelength. The value of α is greater than 10^4 cm $^{-1,}$ that supports the direct band gap nature of the semiconductors .The optical band gap E_g of the prepared thin films was determined by using the following equation [11].

$\alpha h\upsilon = A(h\upsilon - E_g)^n$ --------------------(3)

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 variation of $(\alpha h\upsilon)^2$ versus hυ for the prepared films are illustrated in figure 4. It is clear that the value of E_g decreases from 2.4 ev for MnO_2 thin film to 2.35 ev for MnO_2 3% pb and to 2,3 ev for MnO_2 5% pb thin film.
The extinction coefficient (k) has been calculated using the following relation [12]

$$k = \frac{\alpha \lambda}{4\pi} \qquad \text{--------------------- (4)}$$

Figure 5 shows the spectral dependence of (k) for MnO_2: pb thin films. The value of k increased as the rate of pb increase in the film.

Figure 6 shows maximum value of refractive index (n) for MnO_2 film, when doping by 3% pb there is shifting in long wave NIR. At a result of doping by 5% pb the absorption of thin film increases to maximum value which causes decreasing the reflective value (R) , because of that (R) disappear as shown in Figure 6.
Figure.7 shows the behavior of real dielectric coefficient ε_1, there is a small shift to direction of long wave-length , Figure. 8 shows increasing the value of imaginary dielectric coefficient ε_2 with increasing ratio of doping.

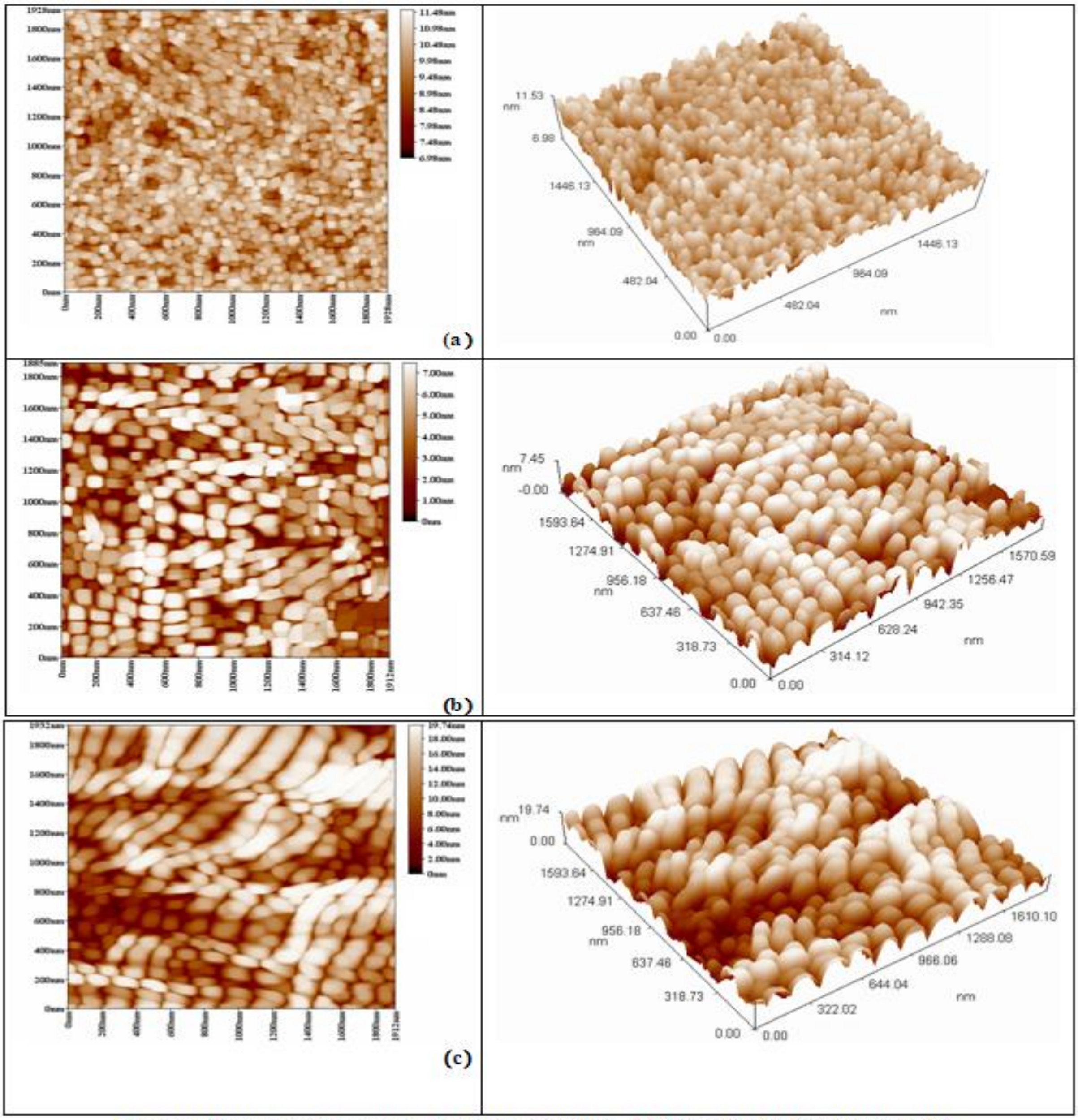


Fig.2: AFM images of prepared thin films: (a) MnO_2, (b) MnO_2:3%Pb, (c) MnO2:5%Pb.

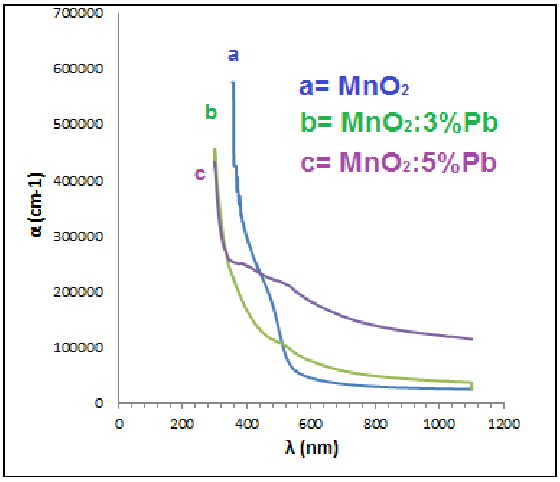
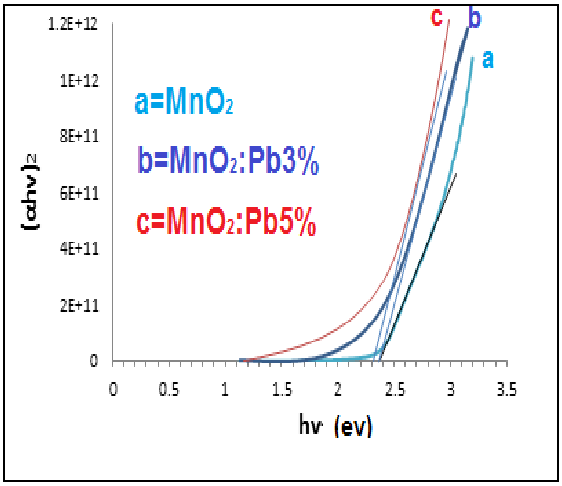
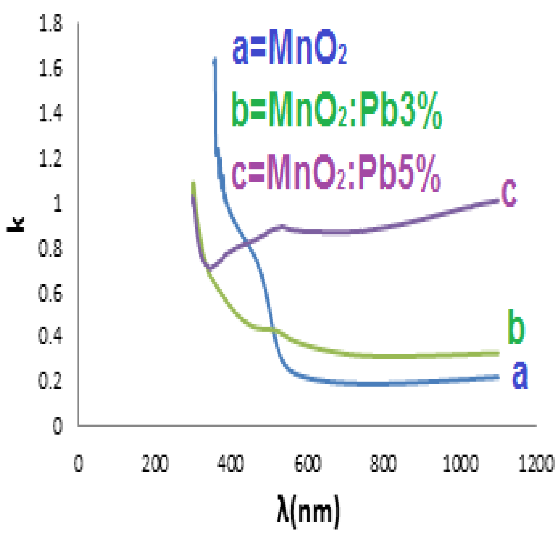


Fig.3: Absorbance coefficient spectra as a function of wavelength for thin films prepared.



Feg.4: Optical energy gap values for thin films prepared.

.



Feg.5: The extinction coefficient (k) as a function of wavelength (λ) for thin films prepared.

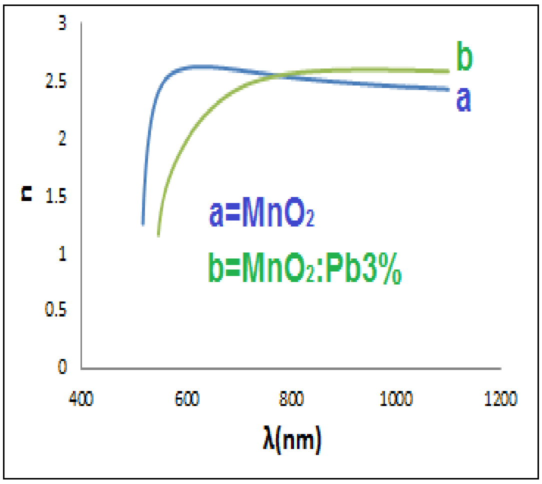


Fig.6 : Refractive index (n) as a function of wavelength (λ) for thin films prepared .

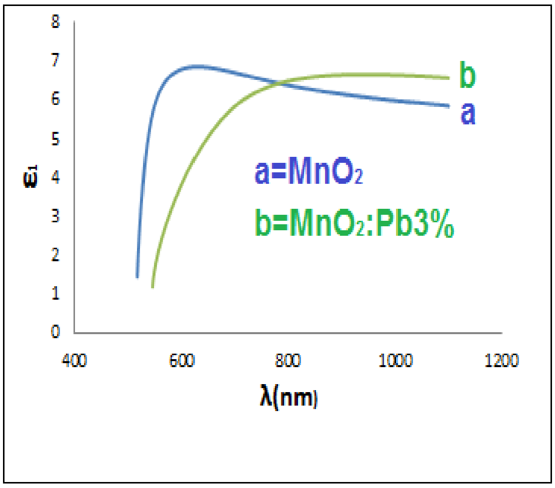
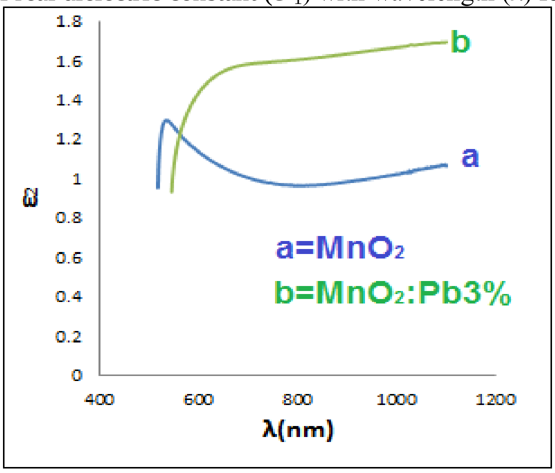


Fig.7: The variation of real dielectric constant (ε_1) with wavelength (λ) for thin films prepared.



Feg.8: The variation of imaginary dielectric constant (ε_2) with the wavelength (λ) for thin films prepared.

IV. CONCLUSION

X-ray investigation shows that MnO_2 and MnO_2: pb are polycrystalline orthorhombic system in (101) direction with grain size of 20 nm for MnO_2, 25 nm for MnO_2:3%Pb and 31 nm for MnO_2:5%Pb. AFM investigation shows a good morphology for film's surface with increasing of the grain size and roughness of surface corresponding to the ratio of doping. The optical measurements indicate that the optical energy gap E_g of prepared films decreased from 2.4 ev to 2.3 ev corresponding to the ratio of pb doping.

REFERENCES

[1] P.U.Asogwa ,S.C.Ezugwu ,F.I.Ezema ,superficies y Vacio 23 (1) 18-22,marzo de (2010).
[2] H.Y.Xu,S.L.Xu,X.D.Li,H.Wangand .Yan, App.Surf.Sci 252,4091(2006).
[3] X. Huang, D. Lv, H. Yue, Attia and Y. ang, Nanotechnology 19,225606 (2008).
[4] P.U.Asogwa,Journal of optoelectronicsand biomedical materials,Vol.2,Issue 3,July-Septemper (2010),p.109-117.
[5] S.Karamat,S.Mahmood,J.J.Lin,Z.Y.Pan,P.Lee,T.L.Tan,S,V,Springham,R.V.Ramanujan,R.S.Rawat,AppliedSurfaceScience 254(2008)7258-7289.
[6] P. Fau, J.P. Bonino, A. Rousset, Applied Surface Science, Vol.78, Issue.2, (1994) pp.203-210.
[7] A.K.M.FaridULIslam,R.Islam,K.A.Khan,Journal of materials science :Materials in electronics 16(2005)203-207.
[8] H.Xia.W.Xiao.M.O.Lai.l.Lu:Nanos-cale es Lett (2009) 4:1035-1040.
[9] Selvaraj Rengaraj, Sun Hee Jee,Selvaraj Venkataraj, Younghun Kim,Selvaraj Vijayalakshmi,Eveliina Repo,Arto Koistinen,and Mika Sillanpaa,Journal of Nanoscience and Nanotechnology Vol. 11,1-10,(2011).
[10] Alaa A.Al-Jubory, International journal of science and technology Vol.2 no.10,707-712,October (2012).
[11] Y.Jayasree, U.Chalapathi, P.UdayBhaskar, V.Sundara Raja,Applied Surface Science 258 (2012)2732-2740.
[12] E.Guneir, A.Kariper ,J.of Alloys and Compounds,516,(2012) 20-26.