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Research Article

EFFECT OF SUBSTRATE TEMPERATURE ON STRUCTURAL AND OPTICAL PROPERTIES OF PbO THIN FILMS DEPOSITED BY CHEMICAL SPRAY PYROLYSIS TECHNIQUE

Abdulazeez O. Mousa and Ali F. Marmoss*

Department of Physics, College of Science, University of Babylon, P.O. Box 4, Babylon, Iraq.

ABSTRACT

Lead oxide (PbO) thin films were deposited onto glass substrates using chemical spray pyrolysis (CSP) technique. The effect of substrate temperature on the structural and optical properties of PbO thin films has been investigated at thickness (177) nm. From the X-Ray diffraction measurement found all the films were polycrystalline in nature with tetragonal and orthrhombic structure corresponding to α -PbO and β -PbO. The films coated at 200 °C and 250 °C were (101) oriented, while the films deposited at 300 °C and 350 °C were (002) oriented. Above 350 °C, the pure tetragonal nature deteriorated and the peaks corresponding to orthorhombic phase were observed. The crystallite size of the films increased from 21.79 nm at (200°C) to 53.14 nm at (300°C) and then decreased with the increasing of substrate temperature. Atomic force microscopic (AFM) measurement showed the grain size ranging of (74.44-120.12) nm. From the UV-VIS we found the band gap of the films increased from (2.31) eV to (2.80) eV with the increasing of substrate temperature.

Keywords: Thin films, PbO, X-ray diffraction, chemical spray pyrolysis technique.

1. INTRODUCTION

Transition metal oxide thin films constitute a very interesting class of materials because of the various properties they exhibited. Mostly studied oxide films usually have wide band gap values. Depending on the preparation conditions, the conductivity of these oxide films varies from insulator to conductor M. Fleischer and H.Meixner (1992). Due to their enhanced optical and electronic properties, the metal oxide based thin films have been used in a wide variety of microelectronic and optoelectronic applications such as electroluminescent devices, magnetic memories and dielectric layers J. H. Hao *et.al* (2004), etc... Among the various transition metal oxide thin films, lead oxide is technologically important due to its attractive properties. Lead oxide thin films with different phases possess multiple levels of reflectance which makes them suitable for optical storage devices S. Chao *et.al*(1990). Among the different phases possessed by lead oxide, lead monoxide (PbO) is an attractive material with low electrical conductivity, interesting semiconducting and photo conducting properties which make it suitable in laser technology and imaging device applications G. Trinquie and R. Hoffmann *et.al* (1984). It also finds applications as semiconducting gas sensors for CO₂ and also as high refractive index materials . PbO thin films have been used as anodic material for lithium secondary batteries M. Martos *et.al* (2001).

The preparation of PbO thin film is often complicated by its high volatility at relatively low temperatures. It has been reported earlier that at low temperature, PbO exist in tetragonal phase (α – PbO) and at high temperature it exist in orthorhombic phase β – PbO. At 490°C under atmospheric pressure, α – PbO undergoes a phase transition to β – PbO. PbO thin films have been deposited by various methods such as metal organic chemical vapor deposition , dc magnetron sputtering , electro-deposition and spray pyrolysis

M. Suganya *et.al* (2014). Among the chemical methods, spray pyrolysis has been proved simple and inexpensive A.R. Balu *et.al* (2012). Although, this technique are very much comparable with low cost, large area coating, minimum wastage and simple apparatus requirements, the microstructural properties of the PbO films deposited by this technique differ remarkably. Considering these factors, in this work PbO thin films were preparated by this technique and the structural, morphological, and optical properties of the films were studied and the results are presented here.

2. EXPERIMENTAL

Lead Oxide thin films have been prepared by (CSP) technique onto highly cleaned glass substrate with the dimensions (2.5 x 2.5) cm. A homogeneous solution of (0.03M) was prepared by dissolving lead chloride compound (PbCl₂.2H₂O), [99%, BDH] by re-distilled water and a few drops of glacial acetic acid were then added to stabilize the solution. The solution was stirred for (1hr) with a magnetic stirrer, the temperatures used in this work were (200, 250, 300, 350, 400, 450)° C. The carrier gas was (compressed nitrogen) and the solution is fed into a sprayer nozzle at a pre-adjusted constant atomization pressure (4.5 bar) and we use (15 No. Of spray) as aconstant thichness (177) nm for all samples . The crystal structure of the PbO thin film was determined by (XRD) using Shimadzu (6000) diffractometer with CuK α X-ray source. Their surface morphology was studied with an (AFM). The optical transmission and reflection spectra are used to study the optical properties of deposit thin films and have been analyzed using UV–VIS spectrophotometer at room temperature.

3. RESULTS AND DISCUSSION

We discuss in this section some properties that descripe characterization of (PbO) thin film deposited by (CSP) technique :

3.1 Structural Properties

Fig. 1 depicts the X-ray diffraction patterns of PbO thin films preparated by the spray pyrolysis technique at various substrate temperatures .The presence of many peaks indicates the polycrystalline structure of the films. Thus, the XRD patterns reveal that the crystallographic properties of the PbO films preparated at low substrate temperatures (up to 250°C) are almost similar, whereas the films coated at higher substrate temperatures (greater than 300 °C) show entirely different and interesting microstructural characteristics. The intensities of the peaks (111) and (112) observed for the films coated below 300 °C are very low and their presence could not be detected for the films coated above 300 °C. The predominance of (002) plane in the films coated at temperatures greater than 300 °C clearly shows that the growth of the crystal is such that the c-axis is perpendicular to the surface of the substrate .

These observations showed that the microstructural properties of PbO films strictly depend on the growth mechanism, which strongly varies with respect to substrate temperature. The value of (002) orientation increases with substrate temperature and attains a maximum value at 300 °C, whereas the value of (101) decreases and attains a minimum value confirming the influence of substrate temperature on the growth mechanism of the as deposited samples. No traces of lead chloride were observed in the films coated between 200 and 350 °C, when substrate temperature was increased to 250 °C, the salts completely decomposed to α -PbO (litharge) with a strong orientation along the (001) plane, This results agree with M.Cruz *et al* (2002).

Above 350 °C, the pure tetragonal nature deteriorated and the peaks corresponding to orthorhombic phase were also observed. Thus, a mixture of both tetragonal and orthorhombic phases was observed for the PbO films coated above 400 °C and the orientation changed to plane corresponding to orthorhombic phase as it is evident from the XRD pattern of the PbO film coated at 450 °C. This phase transition observed at 450 °C strongly favors the fact that α -PbO (tetragonal) undergoes a transition to β -PbO (orthorhombic) at 490 °C this agree with M.A Ying-Ren (1994). All peaks appeared in the XRD spectra are consistent with the International Centre for Diffraction Data (JCPDS) card No. 85-1739 and revealing the tetragonal phase of PbO thin films. It can be concluded therefore,that substrate temperature plays a vital role in the growth mechanism of lead oxide thin films prepared by the spray pyrolysis technique. The crystallite size of the films for the (002) peak, calculated using Debye Scherrer's formula, C. S. Barrett and T.B. Massalski (1966) :

$$D_{S} = \frac{0.94 \,\lambda}{\beta \cos \theta}$$

(1)

Where (β) is the full width at half maximum of characteristic spectrum in units of radians .the average grain size that we found decreased with increasing substrate temperature , the values of (D_s) equal to (21.79, 15.60, 53.14, 34.91, 26.89 and 31.32) nm corresponding to the following substrate temperatures (200, 250, 300, 350, 400, and 450)° C respectively.



Fig. 1: The X-ray diffraction patterns of the prepared films at different substrate temperatures a)200°C, b) 250°C, c) 300°C, d) 350°C, e)400°C, f) 450°C

3.2 Microstructural Properties

Fig. (2) shows a PbO crystal surface imaged with the AFM in the three-dimensional plot. The Van der Waals forces (FvdW) are interactive force acting between tip and sample was estimated by using the following relation:

$$FvdW = HR/6d^2$$
 (2)

Where (H) is the Hamaker constant it's in the order of 10^{-19} J, (R) is the tip radius, and (d) is the spacing between tip and sample. The van der Waals forces are significantly affected by the medium in the gap between tip and sample. The results of an AFM surface roughness analysis of the lead oxide thin films over a scanning area, (2000 nm x 2000) nm are shown in Fig.(2). In this work Fig.(2,a-f) shows the three-dimensional topography of lead oxide films, where roughness are seen with well-defined grains. The roughness gives an impressive insight of the excellent capability of the method to measure surface topography.

To study the changes in roughness of the film, it is very important that the area analysed should remain well adhered to the substrate. It is also important that the area chosen to be the same for all measurements. In order to quantitatively describe the surface morphology, the researchers F. Family and T.Vicsek (1991), A.L.Barabasi and H.E. Stanley (1995) were used to analyse the quantitative information on the surface morphology of AFM data. The amplitude parameters like root mean sequare (RMS), and average eurface roughness are used to evaluate the surface topographical properties. In this work both amplitude and functional parameters are calculated as a function of substrate temperature and are given in Table (1).

We found from the Table (1) that both the (RMS) and surface roughness increased with increasing substrate temperature but the grain size extrapolating from the AFM measurmaents decreased.

3.30ptical Properties

Study of materials by means of optical transmittance provides a simple method for explaining some features concerning the band structure of materials. Optical absorption measurements of PbO films were carried out in the wavelength range (200 – 750) nm. Fig. 3 shows the variation of transmittance with wavelength of the asdeposited PbO samples.

Irrespective of the substrate temperature, a shoulder is noticed at 350 nm for all the films, which corresponds to the fundamental absorption edge due to electron excitation from the valence band to conduction band. The transparency increases with an increase in substrate temperature and attains a maximum value for the film coated at 450°C, and then it decreases. The general increase in the transmittance with decreased film thickness may be attributed to perfection and stoichiometry of the films A. H. Moharram *et.al*(2014) . The low transmittance at temperatures 250, 300 and 350 °C might be due to high thickness obtained for those films, which reflects in the resistivity of the films obtained at those temperatures.

Fig. 4 shows the reflectance variation with the wave length, and its evident the reflectence decreases with an increase in substrate temperature and the average vlue of reflecance in the visible region at the range of wave length (420 – 690)nm ,the high reflectance value of all samples in the UV region at (350) nm of wave length.

Substrate temperatures	RMS (nm)	Roughness (nm)	Average grain size (nm)
200	0.39	0.33	120.12
250	2.90	2.49	98.85
300	0.65	0.54	87.00
350	0.80	0.69	74.44
400	3.85	3.40	100.94
450	1.49	1.25	95.45

 Table 1 : AFM data for (PbO) thin films at different substrate temperatures



Fig. 2: AFM images of PbO thin film at different substrate temperatures a)200 ° C, b) 250° C, c) 300 °C, d) 350° C, e)400° C, and f) 450° C



Fig. 3: Variation of transmitance of PbO thin films with wavelength at different substrate temperatures



ig. 4:Variation of reflectance spectrum with wave length at different substrate temperatures

Fig. 4 is the plot of absorption coefficient with the photon energy for lead oxide thin film under study. The absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semi conductors are employed in the determination of the energy gap, Eg. The energy band gap for the thin film deposited in this work was calculated from The absorption coefficient (α) and the incident photon energy(**hv**) using the relation S.A.Mahmoud *et.al*(2011) :

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

Where (A) is a constant, E_g is the band gap of the material and the exponent (n) depends on the type of transition, n = 1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect, respectively. Taking n = 1/2, the direct optical band gap from $(ahv)^{1/n}$ vs. hv plot. Fig. 5 has been calculated by extrapolating the linear portion of the graph to hv axis. The intercept on the hv axis

gives the direct band gap value. The band gap values were found to be in the range of (2.31 - 2.8) eV. Better crystalline quality due to increased carrier concentration might be the reason for the high value of Eg obtained for the PbO film coated by the spray technique, The band gap values obtained in this work are consistent with the values reported by M. Suganya *et.al* (2015).



Refractive index is one of the fundamental properties for an optical material because it is closely related to the electronic polarization of ions and the local field inside materials. The complex optical constant (refractive index, (n)) of the as-deposited PbO films has been evaluated by the relation M. Suganya *et.al* (2015):

$$n = \left(\frac{4R}{(R-1)^2} - k^2\right)^{1/2} - \frac{(R+1)}{(R-1)} \tag{4}$$

Where (R) is the reflectance, the extinction coefficient, which is related to the exponential decay of the wave as it passes through the medium, is defined asL. Kazmerski and A. Clark (1980) :

$$k = \frac{\alpha \lambda}{4\pi}$$
(5)

The obtained values of refractive index, extinction coefficient of the PbO films are presented in Table (2). The high value of (n) obtained for the PbO film coated at 200°C can be attributed to an increase of its surface roughness which acts to decrease the effective mean free path through increased surface scattering and this fact strongly favors the reason for the reduction of its transparency. This fact is again supported by the high value of "k" obtained for the film coated at 200°C which indicates high absorption and reduced transmittance as the variation in extinction coefficient is paralleled by the absorbance of the PbO films.

Substrate temperatures (ºC)	Energy gap (eV)	Refractive indix	Extinction coeffecient (k X 10 ⁻³)
200	2.31	2.57	16.25
250	2.35	2.55	29.81
300	2.40	2.52	64.05
350	2.62	2.49	64.11
400	2.80	2.45	42.66
450	2 70	2 31	23 97

Table 2: The values of energy gap ,refraive indix and extinction coeffecient of PbO thin film variation with different substrate temperature

It is well known that polarizability of any solid is proportional to its dielectric constant. The real and imaginary parts of the complex dielectric constant are expressed as J.Millman (1979) :

$$\varepsilon_r = n^2 - k^2 \tag{6}$$

and

$$\varepsilon_i = 2nk$$

where (ε_r) and (ε_i) are the real and imaginary parts of the dielectric constants, respectively. The variation of (ε_r) and (ε_{im}) with wavelength of the as-deposited PbO films are shown in Fig. 6 and Fig. 7.

(7)



Fig. 6: Real dielectric constant as a function of wavelength for PbO thin film with substrate temperature





Our values are comparatively good to those reported earlier . The Figs. (6 and 7) show that in all samples the real part(ϵ_r) behaves like the refractive index because of the smaller value of K² compared to n², while the

imagenary part (ϵ_{im}) depends mainly on the K values ,which is related to the variation of the absorption coefficient . This means that real part decreases and the imaginary part increases when substrate temperature increasing.

CONCLUSIONS

PbO thin films have been deposited on glass substrates at different substrate temperatures by the spray pyrolysis technique using lead acetate as the precursor salt. The role of substrate temperature on crystallographic structure and optical properties of the deposited films has been systematically investigated. XRD studies revealed that the PbO films highlight a crystal transition from a preferred (101) orientation corresponding to tetragonal phase at temperatures < 300 °C to a (002) orientation at temperatures > 300 and < 400 °C. A mixture of both tetragonal and orthorhombic phases is observed for the film coated at 350 °C. The preferred orientation changes to (111) plane corresponding to orthorhombic phase for the film coated at 450 °C, which strongly favors the fact that α -PbO will undergo a transition to β -PbO at higher temperatures.From the AFM we found that the grain size decreased from (120.12) nm to (95.45) nm . Film coated at 450 °C has the maximum transmittance of 81 %. The band gap values were found to be in the range (2.31 – 2.8) eV.

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