

Structural, Morphological, and Some Optical Properties of Amorphous and Polycrystalline Lead Oxide Thin Films

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Abstract:

Lead oxide (PbO) thin films were deposited on unheated glass substrates, using the vacuum thermal deposition with a rate of deposition 0.7 nm/ s, at 130nm thickness. The annealing temperature was varied from 523 to 723K for 2 hr. X-ray diffraction (XRD) analysis was used to study the structural and crystallite size of PbO thin film. Before annealing effect, the XRD results indicated that the PbO film is in amorphous nature. After annealing, the corresponding diffraction patterns revealed that the films crystallize in polycrystalline mixed compounds of (PbO_{tet}), and (PbO_{orth}) with a preferred orientation along (020) plane. The average crystallite sizes estimated from XRD data was found to lie in the range of 15.11 – 36.80 nm. The surfaces morphology of these films was studied by the Atomic Force Microscopy (AFM) studies. AFM confirmed that the PbO films have good homogeneous surface. The roughness average, and root mean square values increased with the increasing annealing temperatures. The higher optical transmittance value of PbO film annealed at 523K was found to lie in the range of 88-91% in VIS and IR regions respectively. The optical properties showed that the PbO thin films have allowed direct transitions and the values of energy gap decreased with increasing annealing temperature.

Keywords: Lead oxide thin film, X-ray diffraction, AFM, UV-visible spectroscopy.

Introduction:

Thin Film term is a layer or several layers of atoms for a certain substance whose thickness ranges between (10nm) and less than (1 μ m)[1]. Its conductivity can vary from an insulator to a conductor by the deposited method, substrate, and annealing condition [2]. The technology of thin film deposition gets its development by increasing the performance, reducing the costs and control of characteristics different from the substrate. These features have permitted to development of entirely new products, provided additional features in design and manufacturing, achieved of improved functionality in the products, conserving resources and materials and reduce the wastes encountered in traditional manufacturing. The major area of thin film technology is concerned with the ability to grow an epitaxial film on a substrate. This ability gives an control on the composition and structure as

well as geometrically in which films can be deposited so this modification of devices become easy and economical [3]. Due to their various optical and electronic properties, lead oxide have been used for a wide variety of microelectronic and optoelectronic applications[3], such as electroluminescent device [4], magnetic memory [5], dielectric layer [6], and good material for warming applications in home in temperature regions and in agriculture [7].

Lead oxide may be fatal if swallowed or inhaled. It causes irritation to skin, eyes, and respiratory tract. It affects gum tissue, central nervous system, kidneys, blood, and reproductive system. It can bio accumulate in plants and in mammals [8]. The synthesis of nanostructured lead oxide has an attention. Lead element has a lot of oxide forms, such as

PbO, Pb₂O₃, Pb₃O₄, PbO₂ and phase of α , β [5,6]. Because of lead oxide possess numbers of properties this results several phases of lead oxide caused different levels of reflectance and thin films of lead oxide can be used as optical storage devices[9], and gas

Materials and methods:

Lead monoxide (PbO) was powder materials from Rediel de hien Made by Germany, with high purity (99.9%), color red and density 9.53 g/cm³. The type of substrates was used for depositing thin films by thermal evaporation is glass slides. These are (7.6 × 2.54) cm² in area and 0.12 cm in thickness, which were used to study the structural and optical properties. The cleaning of the substrate is very important because it has a great effect on the properties of the thin films. The lead oxide was prepared by thermal evaporation technique at RT under pressure up to 1×10⁻⁷ mbar with rate of deposition 0.7 nm. sec⁻¹, annealed at annealing temperature 523,623,723K for 2hr and thickness 130nm. The molybdenum boat (trough style boat) was used for deposition of PbO thin films.

X-ray diffraction (XRD) analysis was used to recognize the crystal structure of (PbO) thin films, employing CuK α radiation ($\lambda=1.5418$ Å) with operating voltage 15 KV and a current of 30 mA. XRD data were collected from (2 θ) of (0° – 60°). The morphologies of the prepared PbO thin films were recorded by Atomic Force Microscopy (AFM) supplied by (AA3000, Angstrom Advanced Inc.(USA)). It observes the surface roughness and topography of deposited thin films. To investigate the optical properties of PbO thin films, the absorption spectra of these films have been recorded in the wavelength range (200-1100) nm by using the double beam spectrophotometer (Shimadzu model UV-1800 oA (JAPAN)).

sensors[8]. Thin films of lead oxide can be deposited by thermal vacuum evaporation method and studying the structural, morphological, and optical properties by X-ray diffraction (XRD), atomic force microscopy (AFM), and UV-visible spectroscopy[10].

The lattice constants a and b for tetragonal structure estimated from the relation[11]:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

The lattice constants a, b, and c of orthorhombic structure estimated from the relation[11]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2)$$

The average crystallite size (D), estimated from Scherrer's formula [12].

$$D_{av} = \frac{0.94 \lambda}{\beta \cos \theta} \quad (3)$$

Where : θ is the Bragg diffraction angle, β is the full width of the diffraction line at half – maximum intensity (FWHM).

The dislocation density (δ) was determined by the relation [13]:

$$\delta = 1/D_{av}^2 \text{ (line/cm}^2\text{)} \quad (4)$$

The micro strain (ϵ) was calculated by the formula [13]

$$\epsilon = \beta \cos \theta / 4 \quad (5)$$

The number of crystallites per unit area (N) of the films was determined by the formula [13]:

$$N = t/D_{av}^3 \quad (6)$$

The absorption coefficient (α) can be calculated using the expression [14]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (7)$$

Where: t is the samples thickness .

The optical energy gap (E_g^{opt}) was calculated using the Tauc relation which is given by the formula [14]:

$$\alpha h\nu = A (h\nu - E_g^{opt})^n \quad (8)$$

Where n is an integer depending on the nature of electronic transitions (for the direct allowed transitions n has a value of $1/2$, while for the forbidden direct transitions $n = 3/2$), A is energy dependent constant, h is Planck's constant, and $h\nu$ is the energy of the incident photon.

The X-Ray diffraction analysis with the monochromatic $CuK\alpha$ line ($\lambda = 1.54060 \text{ \AA}$) has been carried out for the thermal evaporated PbO thin films of thicknesses consistently around 130 nm. The structural investigation confirmed that the lead oxide films before annealing are in the amorphous state (i.e. there is no diffraction peaks were observed) as shown in Figure (1). Similar behavior was reported by researcher [15].

The XRD patterns of PbO thin films, compounds with the function of annealing temperatures 523, 623, and 723 K were shown in figure (2a, b and c) respectively. PbO thin films of various annealing temperatures 523, 623 and 723 K exhibit peaks at (15, 17.5, 28.5, 30.2, 35.6 & 48.5), (15.5, 17.6, 28.7, 30, 31.3, 35.7, 39.7, 45.1, 48.5, & 57.6), and (15, 28.1, 30.5, 31.4, 35.5, 46.5 & 48.5) in 2θ which correspond to the miller indices (hkl) produced by the [(010), (001)*, (101)*, (020), (002)* & (112)*], [(010), (001)*, (101)*, (020), (002)*, (112)* (110), (121), (220) & (230)], and [(010), (101)*, (020), (020)***, (002)*, (030) & (112)*] planes respectively. All the observed diffraction peaks of the as synthesized lead oxide samples corresponds to polycrystalline orthorhombic PbO with lattice constant $a = 5.490 \text{ \AA}$, $b = 5.892 \text{ \AA}$, and $c = 4.752 \text{ \AA}$ (JCPDS card file No. 38-1477), and tetragonal PbO with lattice constant $a = 3.972 \text{ \AA}$ and $c = 5.021 \text{ \AA}$ (JCPDS card file No. 05-0561). The calculated lattice parameters a , b , and c for orthorhombic structure obtained from

Results and discussion:

1. X-Ray diffraction (XRD)

the position of the peaks (010) and (020) and (121), $a = 5.306 \text{ \AA}$, $b = 5.9983 \text{ \AA}$, and $c = 4.601 \text{ \AA}$ are in good agreement with bulk PbO taken from the JCPDS card file No. 38-1477. Calculation lattice parameters a , and c for tetragonal structure obtained from the position of the peaks (101), (002) $a = 3.93 \text{ \AA}$ and $c = 5.025 \text{ \AA}$ are in good agreement with bulk PbO taken from the JCPDS card file No. 05-0561. The patterns implied that the material was composed of mixed phases. The orthorhombic PbO peak (020) is dominate. Sharp and intense peaks indicate excellent crystallization of the product. The obtained data are in good agreement with those previously reported in earlier studies [16,17,18].

Generally, it can be noticed from figure(2) that the distinct of the diffraction peaks decreased with increasing annealing temperatures, which leads to increase in the crystallite size as evaluated in Table (1) [18,19]. Additionally, the change in the values of number of crystallites per unit area (N), dislocation density (δ), and micro strain (ϵ) of PbO thin films follow the change that has accompanied the crystallite size under the influence of annealing temperatures,

which is summarized in Table (2).

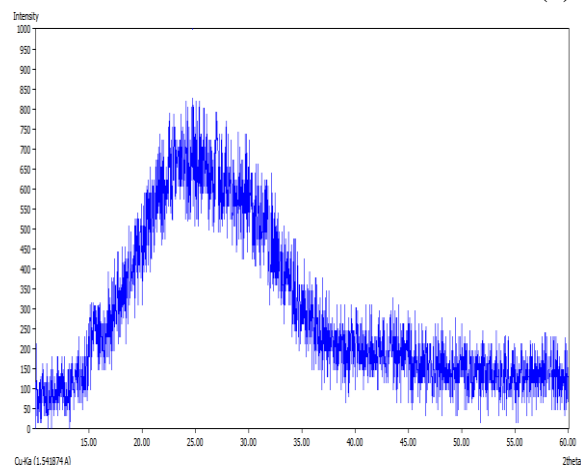


Figure (1): Diffraction spectrum of deposited PbO thin film at thickness $t=130\text{nm}$ before annealing.

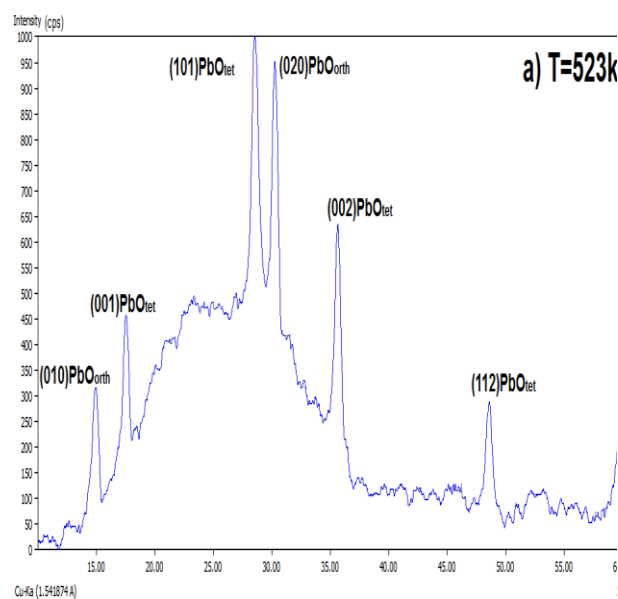
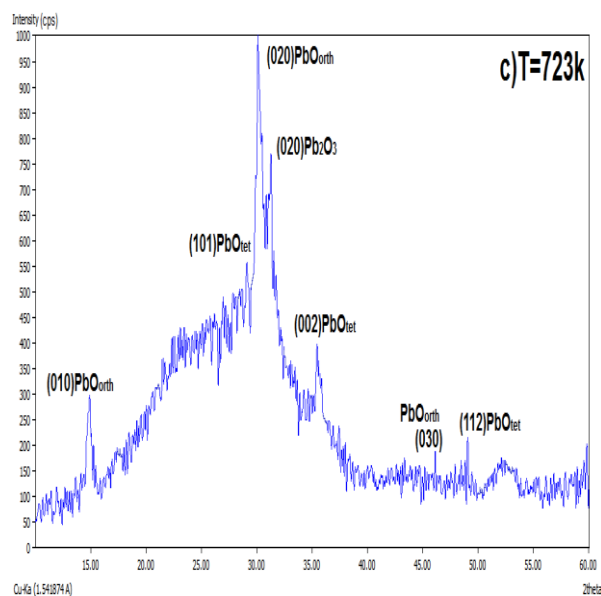
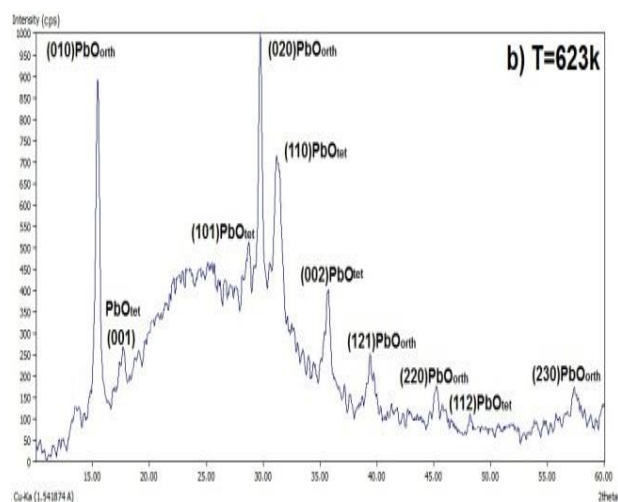


Figure (2): Diffraction spectrum of PbO films deposited at thickness $t=130\text{nm}$ and exposed to



different annealing temperatures ($a=523\text{K}$, $b=623\text{K}$, $c=723\text{K}$).

Sample	(hkl)	2θ (deg)	Θ (deg)	d(nm)	FWHM (deg)	FWHM(rad)	Crystallite size(nm)	Average G.S(nm)
PbO _(t130 nm/T523 K)	(010)	15	7.5	0.589	0.54	0.00942	15.5	15.11
	(001)*	17.5	8.75	0.475	0.5	0.0087	16.79	
	(101)*	28.5	14.25	0.2988	0.65	0.01134	13.15	
	(020)	30.2	15.1	0.273	0.61	0.01064	14.08	
	(002)*	35.6	17.75	0.252	0.55	0.0095	15.9	
	(112)*	48.5	24.25	0.18	0.60	0.0104	15.26	
PbO _(t130nm/T623K)	(010)	15.5	7.75	0.58	0.4067	0.00709	20.59	31.9
	(001)*	17.6	8.8	0.4752	0.233	0.00407	36	
	(101)*	28.7	14.35	0.311	0.2533	0.00442	33.8	
	(020)	30	15	0.273	0.3367	0.0058	26	
	(110)*	31.3	15.65	0.268	0.68	0.011866	12.66	
	(002)*	35.7	17.85	0.254	0.34	0.0059	25.7	
	(121)	39.7	19.85	0.2144	0.22	0.00383	40	
	(220)	45.1	22.55	0.1885	0.4467	0.0077	20.35	
	(112)*	48.5	24.25	0.18	0.13	0.0022	70.25	
	(230)*	57.6	28.84	0.1502	0.28	0.004886	33.7	
PbO _(t130nm/T723K)	(010)	15	7.5	0.589	0.2	0.00349	41	36.8
	(101)*	28.1	14.05	0.2991	0.64	0.011168	13	
	(020)	30.5	15.2	0.277	0.5	0.0087	17	
	(020)**	31.4	15.7	0.284	0.37	0.0064565	23	
	(002)*	35.5	17.75	0.25	0.7	0.012215	12	
	(030)	46.5	23.25	0.197	0.15	0.002617	60	
	(112)*	48.5	24.25	0.18	0.098	0.00171	92	

*// tetragonal

**// Pb₂O₃

star less// orthorhombic

Table (1): X-ray diffraction parameters for (PbO) thin films.

Sample	$N \times 10^{18} (\text{m}^{-2})$	Average $\delta \times 10^{18}$ (m^{-2})	Average ϵ
$\text{PbO}_{\text{t130/T523}}$	0.03768	0.004379	0.24
$\text{PbO}_{\text{t130/T623}}$	0.004	0.0009826	0.13
$\text{PbO}_{\text{t130/T723}}$	0.0026	0.000738	0.158

Table(2): Values of number of crystallite per unit area , dislocation density and micro strain of PbO thin films.

2. Atomic Force Microscopy (AFM)

The surface morphology of the thin PbO films was investigated by tapping mode AFM as a function of annealing temperatures. The typical 2D, 3D, and a diagram of distribution of growth granular groups on the surfaces of the deposited PbO thin films, thicknesses consistently around 130 nm, and annealing temperatures 523, 623 and 723K are shown in figures (3) ,(4), and (5) respectively. The white regions in the figures mentioned represent the formation of agglomerated grains one above the other. Thin films show a uniform granular surface morphology, it can be observed that the roughness and root mean square RMS values of all the PbO films, are increased with increasing annealing temperature. The test results were tabulated in Table 3. These results agree with published study [15], showed increased roughness and RMS with increasing annealing time .

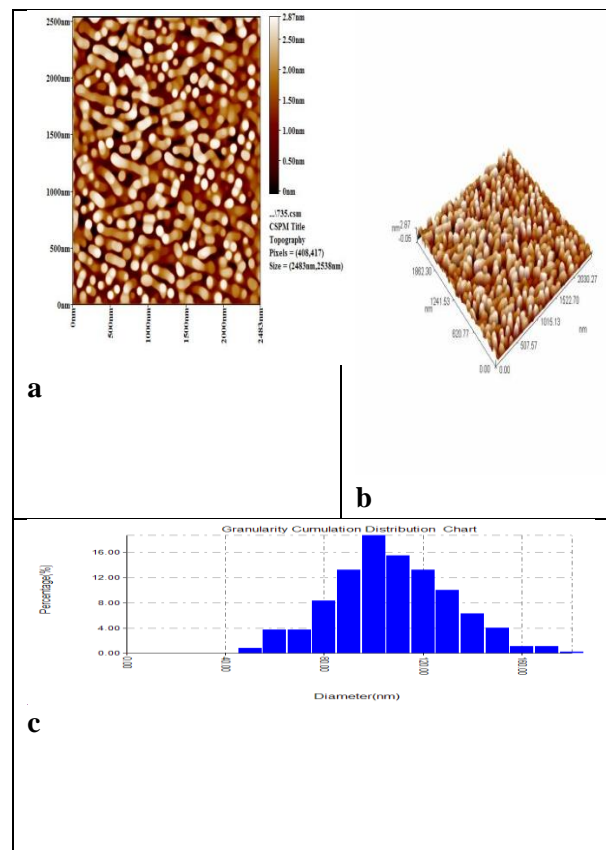


Figure (3): AFM surface morphology of PbO thin film prepared at thickness 130nm with annealing temperature 523K a) 2-D, b) 3-D, and c) granularity distribution.

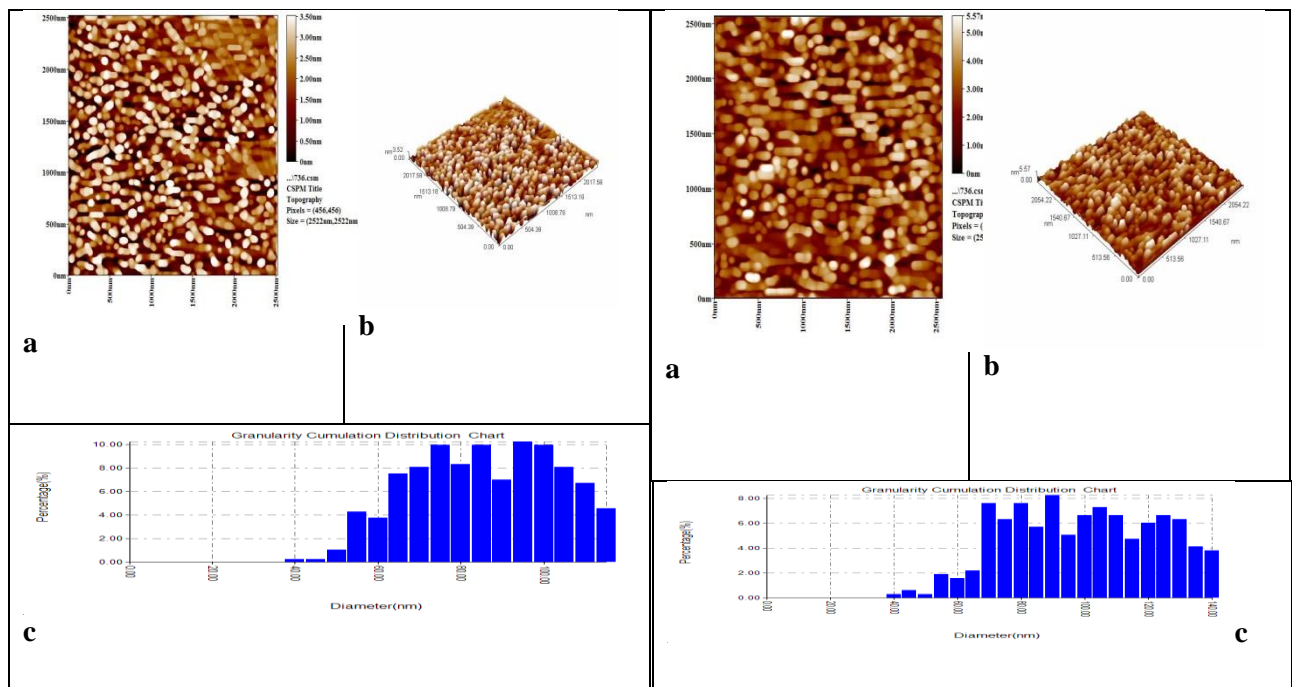


Figure (4): AFM surface morphology of PbO thin film prepared at thickness 130nm with annealing temperature 623K a) 2-D, b) 3-D, and c) granulometry distribution.

Figure (5): AFM surface morphology of PbO thin film prepared at thickness 130nm with annealing temperature 723K a) 2-D, b) 3-D, and c) granulometry distribution.

Sample	RMS (nm)	Roughness (nm)	Average Diameter (nm)	Ten point height (nm)
PbO _{t/130nm} T/523k	0.771	0.656	102.67	1.63
PbO _{t/130nm} T/623k	0.938	0.802	83.03	1.99
PbO _{t/130nm} T/723k	1.14	0.934	96.76	2.91

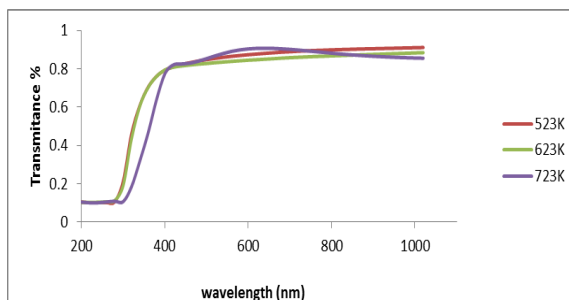
Table (3) Morphological characteristics of PbO thin films at thickness 130nm for different temperature.

3. Optical properties

Lead oxide thin films were examined in transmission using spectroscopy technique as shown in figure (6). An abrupt increase of transmittance with increasing wavelength up to about 400 nm was observed followed by a

slight increase up to 1100 nm. The results show that the transmittance is dependence on annealing temperature. The higher optical transmittance value of PbO film annealed at 523K was found to lie in the range of 88- 91% in VIS and IR regions. The decrease in the transmittance with annealing temperature may have been caused by increase in crystallite size, and the decrease in the number of defects that is associated with high temperature annealing of thin films. The high transmittance in the IR region indicates that PbO films are good materials for warming application; it could be

used as window glazing in homes and in agriculture [18]. These findings are higher than the results of published articles which have studied the compound PbO films prepared in same to our preparation and in other methods too [18,19, 20].



Figure(6): Transmittance spectra as a function of wavelength of PbO thin films for 130nm thickness at different annealing temperature.

The variation of the absorption coefficient (α) versus the energy of incident radiation ($h\nu$) of PbO thin films with annealing temperatures 523,623 and 723K shown in figure (7). The absorption coefficient increased with increasing of annealing temperature for each measuring range. The values of α for all films are multiplied by 10^4 ($\alpha > 10^4 \text{ cm}^{-1}$) in the visible region, which means that the films have a direct optical energy gap [21].

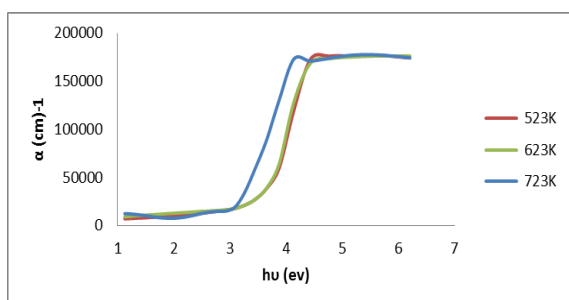
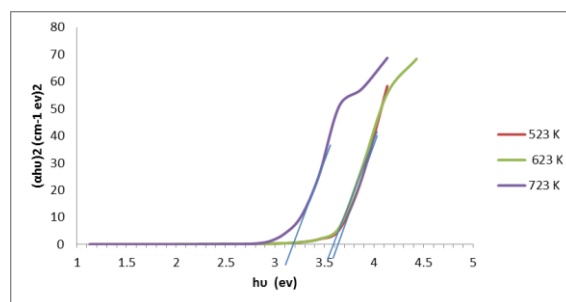


Figure (7): The absorption coefficient and photon energy ($h\nu$) of PbO thin films for 130 nm thickness at different temperature .

The experimental values of $(\alpha h\nu)^2$ plotted against photon energy ($h\nu$) of PbO thin films with annealing temperatures 523,623 and 723K are shown in figure (8). The optical energy gap

E_g^{opt} has been obtained from the intercept of the extrapolated linear part of the curve with the photon energy axis ($h\nu$) at $(\alpha h\nu)^2 = 0$. The linear nature of the plots at the absorption edge confirmed that all deposited films are direct transition type semiconductors. The value of optical energy gap, which have been determined for PbO thin films at $(\alpha h\nu)^2 = 0$, for different annealing temperature 523,623 and 723K were equal to 3.630, 3.580, & 3.190 eV respectively. The results showed that the optical energy gap decreased with increasing annealing temperature. Thus the decrease in energy gap of PbO thin films is due to the increase of the density of localized states inside the band gap[20].



Figure(8): Graphically relation for the allowed direct transition between $(\alpha h\nu)^2$ and photon energy ($h\nu$) of PbO thin films for 130 nm thickness at different temperature

Conclusion

XRD results indicated that the PbO film before annealing is in amorphous nature. After annealing, the corresponding diffraction patterns revealed that the films crystallize in polycrystalline mixed compounds of $(\text{PbO}_{\text{tet}})$, and $(\text{PbO}_{\text{orth}})$ with a preferred orientation along (020) plane. The average crystallite sizes estimated from XRD data was found to lie in the range of 15.11 – 36.80 nm. AFM confirmed that the PbO films have good homogeneous surface. The higher transmittance value of PbO film annealed at 523K was found to lie in the range of 88- 91% in VIS and IR region, Which makes it good materials for warming application; it could be used as window glazing

in homes and in agriculture .The optical energy gap for different annealing temperature 523,623 and 723K were equal to 3.630, 3.580 & 3.190 eV respectively.

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