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Structural and Optical Properties of PbS Thin Films Deposited by Pulsed Laser Deposited (PLD) Technique at Different Annealing Temperature

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Abstract Lead sulphide (PbS) thin films has attracted interest due to its potential applications in optoelectronics devices, gas sensors, solar cell technology and transparent conducting electrodes. Thin films were grown on glass substrates by pulsed laser deposition (PLD) technique at room temperature and different annealing temperatures (573, 673 and 773) K. The structural measurements for PbS thin film show face-centered-cubic structure. Atomic force microscopy (AFM) was used to examine PbS surface. The films exhibit more homogeneity. The root mean square(r.m.s), surface roughness and average grain size were increased After annealing. The optical properties of PbS thin films are studied as a function to wavelength in region (375 - 1100) nm. The optical transmittance of PbS thin films shown that the transparency decreases with increase of annealing temperature. The direct energy gap for PbS thin film was decreases with increasing of annealing temperature for all sample due to the growth of the crystallites. The optical constants such as refractive index, extinction coefficient and dielectric constant were also calculated.

Keywords: *annealing temperature, optical properties of PbS, (PLD) technique*

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1. Introduction

lead sulphide (PbS) is an important direct narrow gap semiconductor material with an approximate energy gap of 0.4 eV at 300K and a relatively large excitation Bohr radius of 18nm[1].Class of semiconductor materials is now occupying an outstanding situation in the basic research and solid state technology. In this category, PbS is a IV-VI compound semiconductor has a cubic lattice with unit cell face center cubic. These properties make PbS very suitable for infrared detection application [2]. This material has also been used in many fields such as photography, Pb^{2+} ions elective sensors and solar absorption [3,4].

In addition, PbS has been utilized as photoresistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings [5]. These properties have been correlated with the growth conditions and the nature of substrates. For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition, spray pyrolysis, photoaccelerated chemical deposition microwave-heating, chemical bath deposition (CBD) [6],and PLD. Furthermore, PLD is more flexible than other conventional techniques, and, it is feasible to control the thickness of films. In the current work, we report the structural and optical properties of PbS thin films on glass substrate grown by PLD method at various substrate temperature [7].

2. Experimental Work

Pbs thin films are prepared by PLD technique. The experiment was carried inside a vacuum chamber at vacuum (10^{-3} Torr) conditions. PbS by BDH chemical Ltd (England) with purity (98%) of these materials were mixed in gate mortar was used to form the target as a disk of 1.5cm diameter and 0.3cm thickness using hydraulic piston type (SPECAC) under pressure of 6 tons for 10 minute. It should be as dense and homogenous as possible to ensure a good quality of the deposit. The nature of the substrate is extremely important because it greatly influences the properties of the films deposited on it. The effectiveness of cleaning of substrates has a strong effect on the adhesion properties of the deposited films. In this work glass slides which were used to study the structural, surface morphology, optical properties of PbS films. the set-up of laser which shows the arrangement of the substrate holders and target inside the chamber with respect to the laser beam. Nd: YAG laser (Huafei Tongda Technology- DIAMOND-288 pattern EPLS) Power= 500 m J, F = 6 HZ, λ= 1064 nm Number of shots = 500 pulse. The focused Nd: YAG SHG Q-switching laser incident beam coming through a window is making an angle of 45° with the target surface.

2.1. Structure and Composition Measurements

2.1.1. X-Ray Diffraction

The structure of PbS thin films grown on glass substrates by PLD method at room temperature and different annealing temperatures, were studied by X-ray diffraction (XRD) techniques using a (Philips PW) X-ray diffractometer system. This system recorded the intensity as a function of Bragg's angle.

The grain size (D) of the crystalline material which, plays the important role in the material properties can be estimated easily from the X-ray spectrum by means of full width at half-maximum (FWHM) method that is often calculated by Scherrer formula;

$$D = \frac{0.94\lambda}{\beta \cos\cos\theta} \quad (1)$$

Where K= 0.9, λ is the wave length of incident X- ray radiation, β is the intrinsic full width at Half Maximum of the Peak, and θ is the Bragg's diffraction angle of the respective XRD Peak.

2.1.2. Atomic Force Microscope (AFM)

The film surface topography of the synthesized was studied To examine the grain size and root mean square of roughness of PbS thin film, an atomic force microscope (AFM) was used. All the samples were studied by taking image for the films surface with tapping mode using atomic force microscope (AA3000 Scanning Probe Microscope SPM. Angstrom Ad-Vance Inc, tip NSC35/AIBS).

2.1.3. Optical Properties Measurements

The optical properties of films on glass Substrat with deposited at room temperature and different annealing temperature at (573, 673 and 773) K have been measured. The optical measurements of thin films depend on, thickness, homogeneity, structure, materials used and the preparation conditions were measured using UV/ Visible SP-8001 spectrophotometer over the range (375-1100) nm. This spectrometer contains two light sources Deuterium and Tungsten lamp within the wavelengths range 190–390 nm and 390–1100 nm of the spectrum respectively. The output data of wavelength, transmittance and absorbance are used in a computer program to deduce the optical energy band gap (E_g) fundamental optical edge and all optical constants. The optical band gab was estimated graphically by applying the Tauce model, the band gap of the deposited material with sharp fall off can be deduced from a plot of the squared absorption coefficient $(\alpha h\upsilon)^2$ versus photon energy (hυ) by extrapolating the straight line of the plot to intersect the energy axis. By measuring the absorbance and transmittance spectra one can measure the absorption coefficient(α), the forbidden energy gap, refractive index(n), extinction coefficient(k), and dielectric constants (the real ε_r and imaginary ε_i) were calculated for these films.

Table 1. Effect of annealing temperature on the structural properties of PbS thin films

Ta (K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl	Phase	card No.
	31.1037	0.4013	2.8731	20.6	2.8582	(111)	Pb	96-900-8478
RT	35.9866	0.6689	2.4936	12.5	2.4753	(200)	Pb	96-900-8478
	52.1070	0.6020	1.7538	14.7	1.7503	(202)	Pb	96-900-8478
	62.0067	0.5351	1.4955	17.3	1.4926	(311)	Pb	96-900-8478
	65.0836	0.5351	1.4320	17.6	1.4291	(222)	Pb	96-900-8478
	25.9532	0.2676	3.4304	30.5	3.4246	(111)	PbS	96-901-3404
573	29.9666	0.6020	2.9795	13.7	2.9657	(200)	PbS	96-901-3404
	43.0100	0.8695	2.1013	9.8	2.0971	(202)	PbS	96-901-3404
	50.9699	0.6020	1.7903	14.6	1.7884	(311)	PbS	96-901-3404
	53.3110	0.6689	1.7170	13.3	1.7123	(222)	PbS	96-901-3404
	25.9532	0.2676	3.4304	30.5	3.4246	(111)	PbS	96-901-3404
673	30.0334	0.4682	2.9730	17.6	2.9657	(200)	PbS	96-901-3404
	42.8763	0.5351	2.1075	16.0	2.0971	(202)	PbS	96-901-3404
	51.0368	0.5351	1.7881	16.5	1.7884	(311)	PbS	96-901-3404
	53.4448	0.4683	1.7130	19.0	1.7123	(222)	PbS	96-901-3404
	25.9511	0.2610	3.4306	31.3	3.4246	(111)	PbS	96-901-3404
773	30.1003	0.2675	2.9665	30.8	2.9657	(200)	PbS	96-901-3404
	42.8700	0.4013	2.1078	21.3	2.0971	(202)	PbS	96-901-3404
	51.0355	0.3345	1.7881	26.3	1.7884	(311)	PbS	96-901-3404
	53.5086	0.4014	1.7111	22.2	1.7123	(222)	PbS	96-901-3404

3. Results and Discussion

3.1. Structural Properties

PbS thin film were deposited on glass substrates prepared by PLD. XRD give the confirmation of presence of Pb in the prepared film as shown in Figure 1. It is seen that Pb exists at room temperature which are distinct peaks in (31.10º, 35.98º and 52.10º) values respectively. The films were fabricated at the lowest temperature have the least crystalline quality as was observed in XRD patterns, but at the higher temperature gained better crystallinity. Figure 1 shows the typical XRD pattern of the PbS thin film samples for different annealing temperatures (573,673,and 773) K. It shows several five diffraction peaks at 2θ values of (25.95º, 29.96º, 43.01º, 51.03º and 53.31º). These were assigned to the diffraction lines produced by (111), (200), (220), (311) and (222) planes of the face-centered-cubic structure of PbS confirmed by standard ASTM data. XRD patterns of all the PbS thin films showed sharp (111) and (200) peaks along with minor peaks of (220), (311), and (222) planes corresponding of the deposited PbS films were calculated and the results were reported in Table 1. For all the films the preferential orientation value of (111) plane has the highest value compared to that of the other planes indicating a strong orientation growth along that plane. This result on preferential orientation is strongly supported with earlier report Mohammad and Rajashree [8,9]. The variation in preferential orientation factor d_{hkl} for (111) as a function of annealing temperature shown in Figure 1, predicts that (111) is maximum for the film coated at (773)K, indicating better crystallinity. These XRD results confirm the proper phase formation of the PbS films. The crystallographic structure of the prepared PbS thin films was determined using a high resolution X-ray diffractmeter. No other peaks are detected in the XRD pattern, confirming high purity of the PbS thin films. The intensity of the peaks increases with increase in annealing temperature which reveals that crystallinity of the film improves with increase in annealing temperature. The crystalline grain size (D) of the PbS films was determined with the Scherrer formula. This effect can be related to the increase of grain size with increasing annealing temperature this result was in agreement with Jana and Laxmi [10,11].

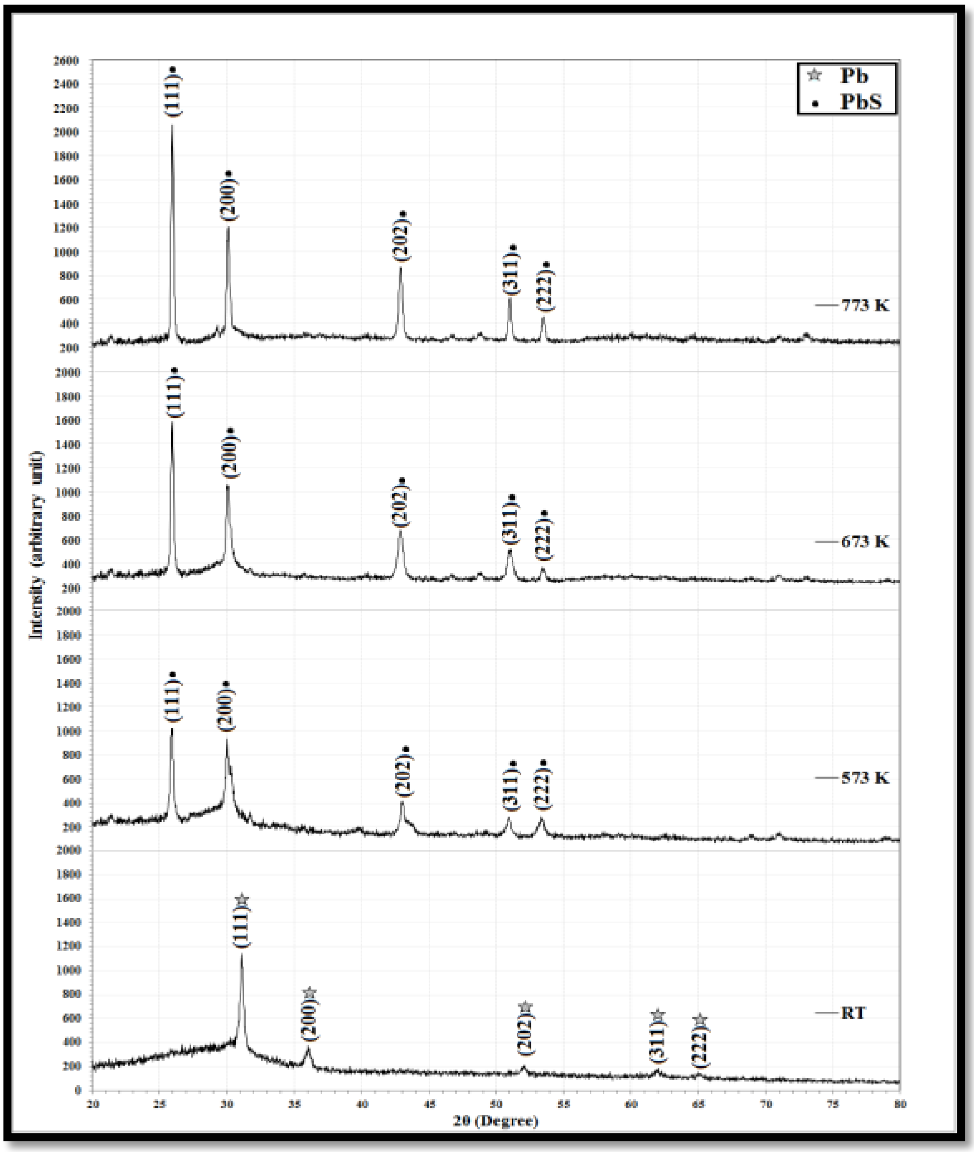

Figure 1. The XRD of PbS thin films at different annealing temperatures (RT, 573, 673, and 773) K

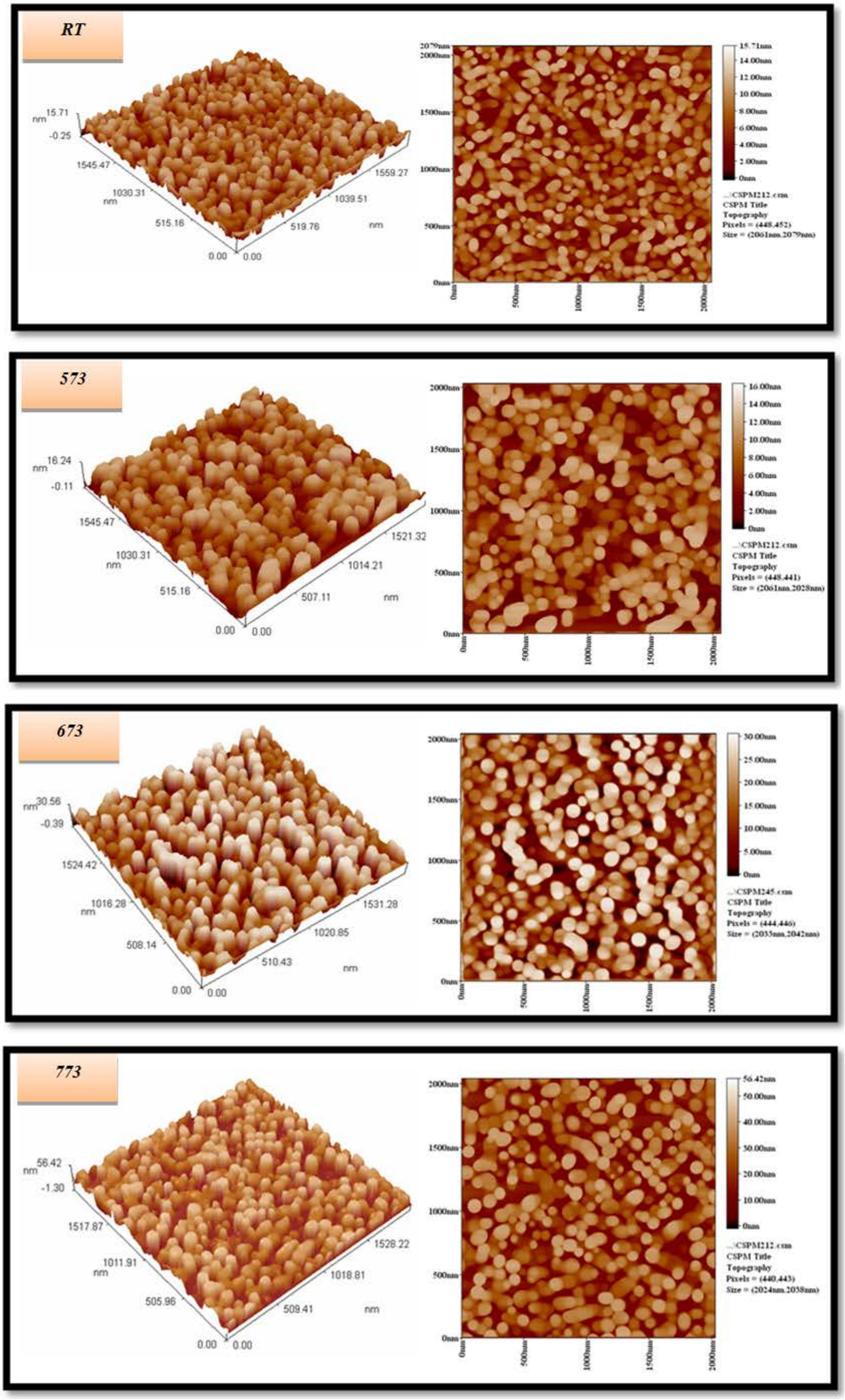

Figure 2. 2D and 3D AFM images pure PbS thin films

Table 2. Morphology Parameters for PbS thin films

Sample	Ta (K)	Average diameter (nm)	Average roughness (nm)	Peak –Peak (nm)	r.m.s (nm)
PbS	RT	77.08	2.34	12.2	2.71
	573	96.12	2.62	11	3.07
	673	97.16	6.77	28.7	7.9
	773	110.44	8.34	31.3	9.53

3.1.2. Atomic Force Microscope (AFM) Analysis

AFM studies reveal that there is a dramatic change in the morphologies of the deposited PbS thin films on glass substrates at different annealing temperatures (573, 673, and 773) K. AFM images of the surface morphology recorded on samples of the PbS thin films deposited are shown in Figure 2. AFM parameters contain average diameter, average roughness, average root mean square (r.m.s) roughness and peak –peak value of experiments and the data of results observed in these experiments were collected for these samples have been shown in Table 2. A dense surface of the thin films was obtained at all cases. The thin films were composed of multilayered grains. AFM images showed the grain diameter of PbS as function of different annealing temperature, it is appears that the particle size increased with increasing of the annealing temperature. The same relation between the average roughness, average (r.m.s) roughness and peak -peak value and the annealing temperature has been observed. In addition, preferential film growth improved with increasing annealing temperature which was in accordance with XRD analysis.

3.2. Optical Properties

In this work we study the influence of the annealing temperature on the optical properties of PbS thin films at deposited on glass substrates by PLD. The first part will be devoted to the study the transmittance. The second will proceed in energy gap of PbS thin films. The third part will proceed in determine the refractive index, the extinction coefficient, dielectric constant, and optical constant measurements at near normal incidence were performed over a spectral ranging between (375- 1100)nm on PbS thin films deposited on glass substrate at room temperature and different annealing temperatures.

3.2.1. The Transmission Spectrum (T)

The transmission of PbS thin films which deposited on glass substrates were determined optical spectra for a series of films were carried out with a UV-VIS-NIR spectrophotometer in the range of (375–1100)nm prepared at room temperature and different annealing temperatures (573, 673, and 773) K by PLD is over 60 %. Figure 3 show that the transparency decreases with increase of annealing temperature because of the increasing thickness with temperature and the transmittance increase with increasing wavelength but is low for wavelength smaller than (600) nm. This result is comparable to one which reported by researchers Yasmeen and Jana [7,10]. As it is clear from spectra, the films have a steep optical absorption feature, indicating good homogeneity in the shape and size of the nanocrystalline and low defect density near the band edge. This is in agreement with the results obtained by Srinivasan [12].

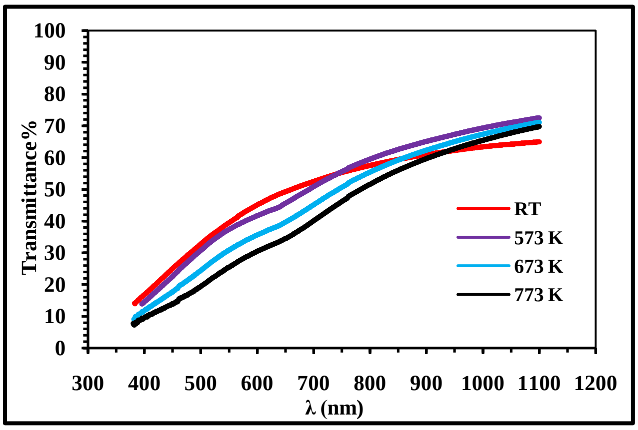

Figure 3. The Variation of the Transmittance with Wavelength of the PbS Films with Different Annealing Temperatures.

3.2.2. Optical Energy Gap (Eg)

Energy gap *(E_g)* is the separation between valance and conduction bands of semiconductor. Variation of $(\alpha h\nu)^2$ as a function of photon energy (h*ν*) is plotted in the Figure 4. As observable, $(\alpha h\nu)^2$ varies linearly with (h*ν*) after a certain amount of photon energy, confirming the direct nature transition mode in the PbS films. The E_g can be obtained by extrapolating the straight-line portion of graph to zero absorption coefficient with deposition at different annealing temperatures (573, 673, and 773) K. It is observed from the Table 3 the E_g values of PbS films decreases with increase annealing temperature which lies in the red region of the visible spectrum due to agglomeration of the Nano-crystallites into larger crystallites. This is an agreement with the results obtained by Rajashree and Thangavel [9,13].

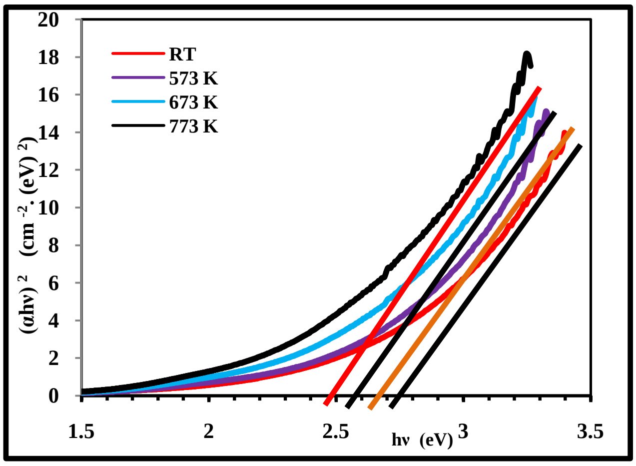

Figure 4. $(\alpha h\nu)^2$ as a function of hν for of the PbS Films with Different Annealing Temperatures

Table 3. Optical Energy gap with Different Annealing Temperatures

Ta K	RT	573	673	773
Eg (eV)	2.71	2.63	2.52	2.45

These values are greater than the bulk material [19]. It may be due to the fact that the amorphous or nanocrystalline films show energy gap higher than of the corresponding bulk materials. The increase in the E_g is due the Nano-crystalline nature of the PbS thin film. This is in agreement with the results obtained by Hussain, ALI and Uhuegbu [14,15,16].

3.2.3. Absorption Coefficient (α)

The fundamental absorption edge of the PbS films, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical energy gap, the absorption coefficient α was determined from the region of high absorption. Figure 5 show the optical absorption coefficient as a function of incident wave length on PbS films at room temperatures and different annealing temperatures (573, 673, and 773) K. It is noticed from these figures that α increases with increasing of annealing due to the decreasing of energy gap. We can evidently see that thin film In the shorter wavelength the absorption coefficient exhibits high values of ($\alpha > 10^4$ cm^{-1}) which causes the increase of the probability of the occurrence direct transitions and then α decreases with increasing of wavelength. The values of the absorption coefficient are nearly in agreement with values reported by Yasmeen and Srinivasan [7,12].

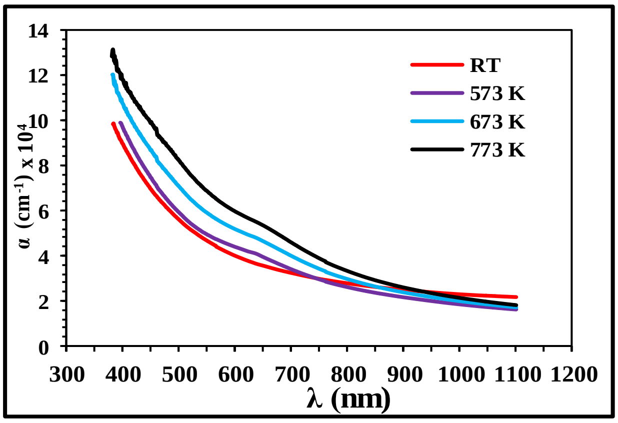

Figure 5. The Absorption Coefficient α for PbS Films with Different Annealing Temperatures

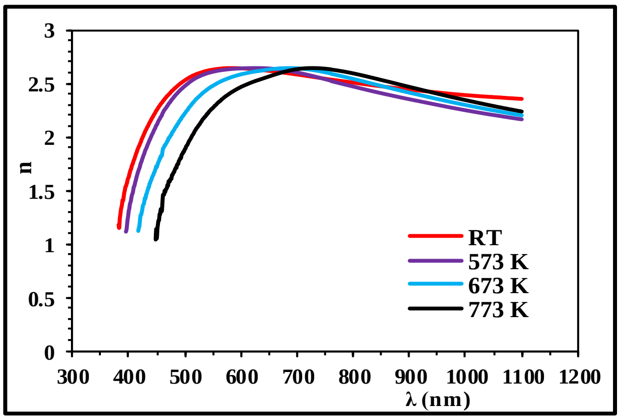

Figure 6. The Variation of The Refractive Index (n) With Wavelength of PbS Films with Different Annealing Temperatures

3.2.4. Refractive Index (n)

The refractive index is the ratio between speed of light in vacuum to its speed in material which doesn't absorb this light. The variation of the refractive index versus wavelength in the range (375-1100) nm at room temperature and different annealing temperatures have been depending on the reflectance values is shown in Figure 6. The maximum value of n for all films is approximately equal the value of (2.6) and we can notice from these figures that the refractive index in general decreases slightly with increasing of annealing temperatures. It is clear from the graph n value decreasing with increasing (λ) after maximum peak with a different manner. The explanation of this behavior may be related to the polarization of thin film because n depends on material polarization where with increasing polarization the velocity of light was decreased so n changed. The polarization depends on crystalinity and on grain size of thin film so these depend on preparation conditions. This is in agreement with Vinodkumar and El-Desoky [17,18].

3.2.5. Extinction Coefficient (k)

The behavior of the extinction coefficient (k) is nearly similar to the corresponding absorption coefficient. Figure 7 shows the extinction coefficient as a function of wavelength for PbS films at room temperature and different annealing temperature. We can observe from the Figure 7 and Table 4 that the extinction coefficient, in general, increasing with increasing of annealing temperature for all films. This is attributed to the same reason mentioned previously, decreases the optical energy gap as a result of absorbance increment. This result agrees well with literature Abbas [19].

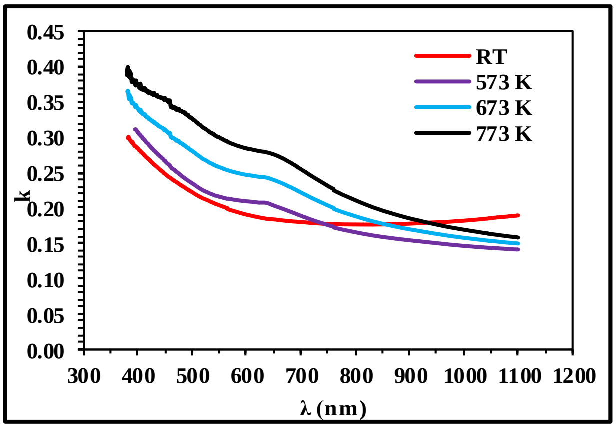

Figure 7. The Variation of The Extinction Coefficient With Wavelength of PbS Films with Different Annealing Temperatures

Table 4. Values of Refractive index (n), Extinction coefficient (k), Real (εr) and Imaginary (εi) Dielectric Constant for PbS films (at 500 nm wavelength)

Ta (K)	T%	α (cm^{-1})	K	n	ε_r	ε_i	E_g (eV)
RT	32.75	55807	0.222	2.530	6.350	1.124	2.71
573	30.73	59004	0.235	2.476	6.076	1.163	2.63
673	24.43	70470	0.281	2.221	4.855	1.246	2.52
773	19.42	81936	0.326	1.886	3.450	1.230	2.45

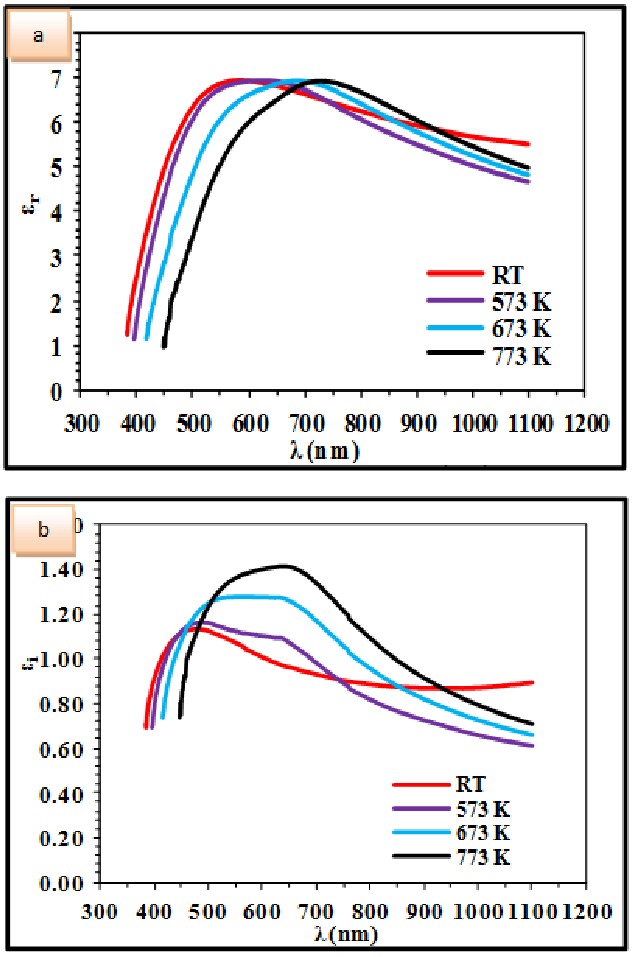

Figure 8. The Variation of The Dielectric Constants a-real part (ε_r) and b- imaginary (ε_i) parts With Wavelength of PbS Films with Different Annealing Temperature

3.2.6 Dielectric Constant

Real and imaginary part of dielectric constant values versus wavelength in the range of (375–1100) nm for PbS thin film with different annealing temperatures. The plots of real and imaginary part of all samples were illustrated in Figure 8(a,b). Figure 8(a) show that all samples behave like the refractive index samples because of the smaller value of (k^2) compared with (n^2), Figure 8(b) shows that all samples behave like the extinction coefficient samples which means that the real and imaginary part increased with increasing of annealing temperatures. It is seen that the real part of dielectric constant decreased by increasing wavelength and the values of real part is higher than imaginary part as shown in Table 4. These measurements are agreed with the data of M.Abbas [20].

4. Conclusions

PbS Thin film were deposited on glass substrates are prepared by means of simple and low cost by PLD technique. Post-annealing process helps to improve the crystalline quality thin films. The effect of growth temperature on structural and optical properties was studied. The typical XRD pattern of the PbS samples for different annealing temperatures show planes of the face-centered-cubic structure. The transmission of PbS thin films which deposited on glass substrates were determined is over 60 %.The band gap energy values of thin films decreases with increase annealing temperature which lies in the red region of the visible spectrum due to agglomeration of the Nano-crystallites into larger crystallites.

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