Synthesis of PbS Thin Film by Chemical Bath Deposition Method and it's structural-Optical Studies

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ABSTRACT: In the present article, we prepared a PbS Thin film by varying its physical parameters such as temperature of the solution, deposition time and concentrations and studied its structural and optical properties. Here, the PbS thin film was prepared by chemical bath deposition route. The structural behavior such as crystallite size, orientation, lattice spacing and strain broadening was also calculated. Using XRD, the PbS thin film shows cubic structure with average crystallite size is 30.04 nm for 45 ºC and 31.07 nm for 65 ºC respectively. The optical properties of PbS thin film were studied using UV-Visible spectroscopy and reported its value subsequently. Such kind of thin film based on PbS compound are useful to increase the efficiency of energy conversation in solar cell areas.

Keywords: *Chemical Bath Deposition, PbS Thin Film, XRD, UV-Visible spectroscopy, W-H Plot.*

I. INTRODUCTION:

Nanocrystalline inorganic materials has been widely studied for solar cell applications, because of their structural, electrical, and optical properties due to quantum confinement [1]. Semiconductor nanoparticles (NPs) have good optical as well as electronic properties, and it has interested to synthesis and characterization of sulfide nanoparticles. Lead sulfide (PbS) is one of them to show a superior optical and electronic properties. PbS is a semiconducting material belongs to the category of *IV-VI* which has an approximate band gap range is 0.37-0.41 eV at 300k [1,2]. According to their narrow band gap, it possesses special optoelectronic properties and found wide applications in optical communication apparatus, radioactivity detector and optical information storage etc. [2]. This kind of materials are widely used in many areas such as photography, Pb^{2+} ion, selective sensors and solar absorption. In addition, PbS has also been utilized as a photo resistance, diode lasers, humidity and temperature sensors as well. As compared to bulk PbS, the Thin film gives very good photovoltaic properties which is already reported earlier [3,4]. PbS thin film is the prominent candidate which effectively used to detect a NO_2 gas at low ppm level [2,5]. For the application of IR detector, Solar absorber, Telecommunication, Amplification, electronic devices, LED's, and Optical switches, the researchers are trying to developed a various property of PbS thin films [6-8]. Nevertheless, PbS thin film are also useful for photography, humidity and temperature sensor [9,10]. PbS based Quantum Dot Solar Cells (QDSCs) are fabricated by QD inks pre-exchanged with different ligands using single-step deposition method [11]. Dopant are plays an crucial role and the PbS:Sr thin film are also used as a Solar absorber for solar cell application [12]. There are various synthesis routes to prepared a PbS NPs and PbS thin film which possibly used tailored applications as per there significance properties [13-17]. However, the above-mentioned synthesis routs are quite difficult, expensive and time consuming. Hence, instead of these routes, we used a promising, simple, and low-cost techniques for the preparation of PbS thin film i.e., Chemical bath deposition (CBD) [4,5,7,8]. CBD is an emerging route which brings the possibility of controlling the PbS films thickness and crystallinity, because of the continuous deposition of multi layers for optical and solar devices. Nevertheless, CBD is also most convenient and frequently used deposition technique to grow PbS thin film.

In our present work, we prepared a PbS based thin film by CBD routes and reported its structural as well as optical properties. Here, we studied six different atmospheric (i.e., for different temperature conditions) prepared PbS samples for structural analysis. Subsequently, we also reported the optical studies for selected PbS thin film samples which briefly discussed in particular subsection.

II. EXPERIMENTAL PROCEDURE:

Here, we prepared a PbS thin film by CBD method. We used a AR graded chemicals such as 0.175 M concentration of Lead Nitrate ($Pb(NO_3)_2$, 0.55 M concentration of Thiourea ($SC(NH_2)_2$), and 0.15 M concentration of Sodium Hydroxide (NaOH) for the preparation of PbS material. In initial stage, we dissolved a $Pb(NO_3)_2$ compound in 30 ml of double distilled water under continuously stirring condition with rotation rate is 340 rpm under 40 ^oC. Subsequently, 30 ml NaOH was added in $Pb(NO_3)_2$ and stirred it for 20 min. After well mixing of above two chemicals, we added 30 ml $SC(NH_2)_2$ and stirred it again couple of minutes. Then ultrasonically cleaned glass substrate dipped in the above mixture solution. The deposition was allowed for 20 min and then cleaned that substrate with DDW. Finally, the prepared light black color PbS thin film are used for further studies. Similarly, we also prepared five more PbS based thin film samples under 45 ^oC, 50 ^oC ^oC, 60 ^oC, 65 ^oC, and 75 ^oC temperature condition, respectively.

The following is the chemical reaction for preparation of PbS material-

$$Pb(NO_3)_2 + 2NaOH \longrightarrow Pb(OH)_2 + 2NaNO_3$$

$$Pb(OH)_2 + 4NaOH \longrightarrow Na_4Pb(OH)_6$$

$$Na_4Pb(OH)_6 \longrightarrow 4Na^+ + HPbO_2^- + 3OH^- + H_2O$$

$$SC(NH_2)_2 + OH^- \longrightarrow CH_2N_2 + H_2O + SH^-$$

$$HPbO_2^- + SH^- \longrightarrow PbS + 2OH^-$$

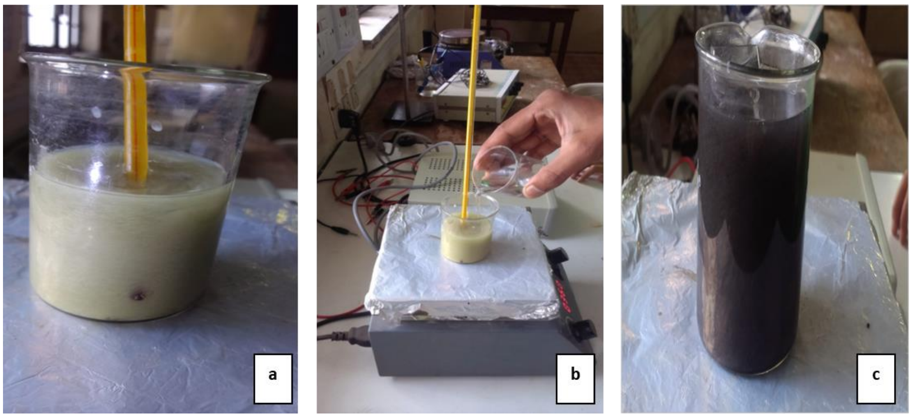

Figure 1: Preparation PbS thin film

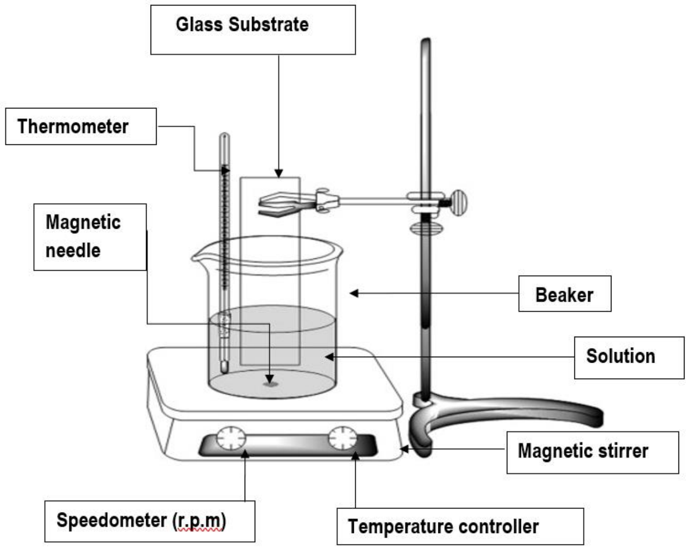

Figure 2: Schematic layout of chemical bath deposition method.

III. RESULTS AND DISCUSSION:

X-RAY DIFFRACTION:

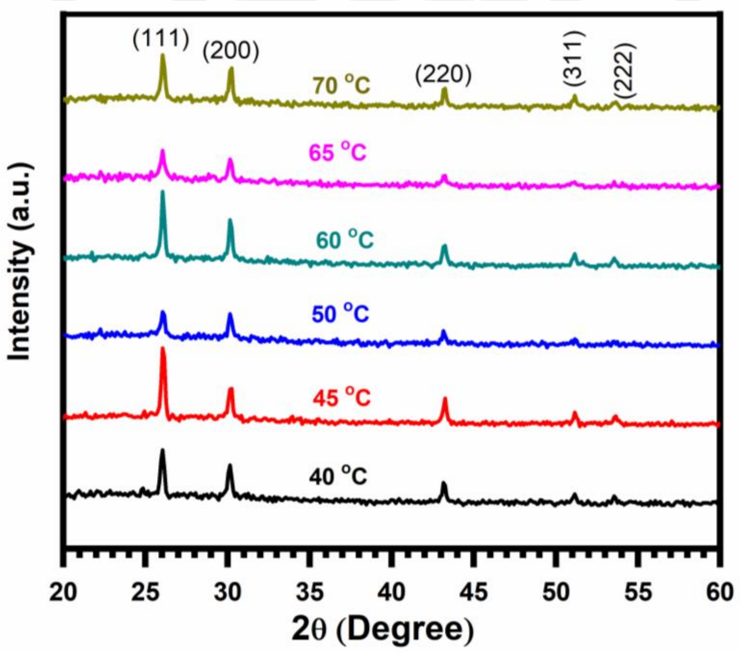

Figure 3: The different temperature condition prepared XRD spectra of PbS based thin film.

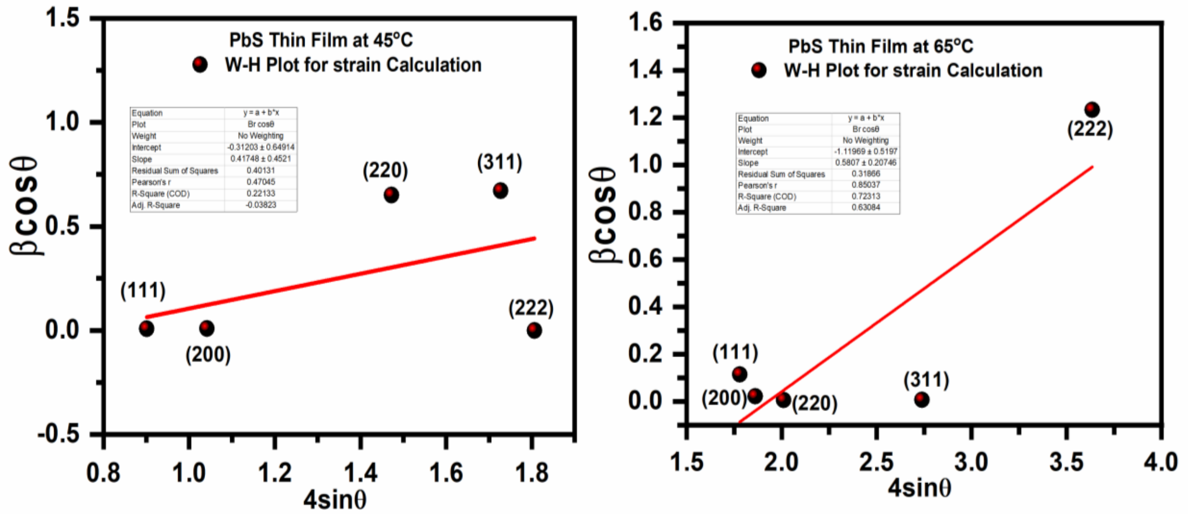

Figure 4: The W-H plot of PbS thin film prepared at 45 °C and 65 °C.

The structural properties of PbS thin film are studied by XRD spectroscopy. The XRD spectrum was recorded in the 2θ range of 20°-60° and found five prominent hkl peaks. The obtained hkl peaks are 26.05°, 30.14°, 43.16°, 51.15°, and 53.65° with their corresponding planes of (111), (200), (220), (311), and (222) respectively (shown in Fig. 3). The PbS thin film shows cubic structure having average crystallite size is ~30.04 nm for 45 °C prepared samples and ~31.07 nm for 65 °C prepared samples. From XRD, we also observed that the *hkl* peak broadening decreases with respect to temperature which is clearly seen in Fig. 3 as well. Moreover, for the determination of this changes, we draw a Williamson-hall (i.e., W-H plot) plot as shown in Fig. 4. The fitting of R-square value values is very less for 45° prepared PbS thin film sample than 65° sample. The lattice strain was also change with respect to temperature which we obtained by W-H plot [18]. However, the calculated value of interplanar distance *'d'* and average lattice constants *'a'* has mentioned in the Table 1.

Table 1: The calculated value by W-H plot of PbS based thin films.

Sample	Plane	2θ	Sinθ	d_{hkl} (Å)	a (Å)	Average 'a' (Å)
45 °C	111	26.0533	0.2254	3.4150	5.9000	5.9040
	200	30.1428	0.2600	2.9615	5.9200	
	220	43.1599	0.3677	2.0940	5.9114	
	311	51.1500	0.4316	1.7840	5.9000	
	222	53.6485	0.4512	1.7065	5.8889	
65 °C.	111	26.05826	0.2224	3.415446	5.9157	5.8882
	200	30.1769	0.2603	2.958013	5.9160	
	220	43.21069	0.3682	2.091191	5.9145	
	311	51.5302	0.4346	1.771407	5.8750	
	222	54.2340	0.4558	1.689304	5.8196	

For 45° and 65° prepared PbS thin film sample, we also calculate the value of strain (ε) and dislocation density (ϱ) for most abundant plane 111, 200, 220 of PbS thin film. The average dislocation density slightly increases with temperature are shown in Table 2. The dislocation density is a measure of the number of dislocations in a unit volume of a crystalline material.

Table 2: The calculated value of strain (ε) and dislocation density (ϱ)

Temp.	Plane	2θ	cosθ	$\beta \times 10^{-3}$	D (nm) Value	Strain(ε) $X\ 10^{-3}$	Dislocation density(ϱ) $x10^{-3}$ nm^{-2}	Average 'ϱ' $x10^{-3}$ nm^{-2}
45 ^{0}C	111	24.5098	0.9772	4.4353	32.08	1.08	0.97	~ 0.99
	200	30.1535	0.9665	4.7140	30.45	1.13	1.08	
	220	43.1590	0.9299	4.5772	32.56	1.06	0.94	
65 ^{0}C	111	26.0477	0.9742	4.7760	29.78	1.16	1.13	~ 1.17
	200	30.1496	0.9655	4.4901	31.96	1.09	0.98	
	220	43.1539	0.9299	5.2502	28.39	1.22	1.24	

UV- Visible Spectroscopy:

Using the UV-absorption spectroscopy, we obtained an absorption spectrum for two thin film samples i.e., a) prepared under 45 °C and b) prepared under 65 °C, shown in Fig. 3. However, we also calculate a band gap energy (eV) was determined by extrapolating the straight-line portion to the energy axis for zero adsorption coefficient α. Hence, the calculated band gap energy is 2.14 eV for 45 °C and 2.27 eV for 65 °C PbS thin film samples (shown in inset image of Fig. 5). Actually, the relation of band gap was inversely proportional to temperature in semiconductor but we found a surprising result here. It maybe happened due the more energy absorbed by higher temperature prepared PbS thin film.

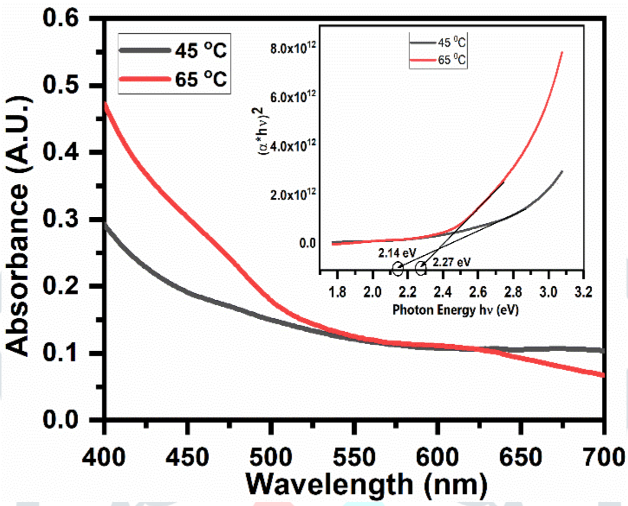

Figure 5: The UV-Visible spectrum of 45 °C and 65 °C temperature thin film prepared PbS samples.

IV. Conclusion:

In overall, we prepared six samples of PbS thin film by CBD route and studied its structural as well as optical properties. Using XRD, we obtained cubic structure along with crystallite size is ~30.04 nm for 45 °C prepared samples and ~31.07 nm for 65 °C prepared samples. However, we also successfully studied and reported the Williamson-Hall analysis for better understanding of lattice strain broadening and hence, the average observed value is 5.9040 for 45 °C prepared PbS thin film and 5.8882 Å for 65 °C, respectively. Moreover, we also calculate the band gap energy for both the samples and the value is 2.14 eV for 45 °C and 2.27 eV for 65 °C PbS thin film. Hence, this kind of PbS thin film material maybe useful in the areas of heterojunction solar cells, humidity and temperature sensor etc.

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REFERENCES:

[1] Ahmed.S. Obaid (2012). Preparation of chemically deposited thin films of CdS/PbS solar cell. Superlattices and Microstructures, 52(4): 816-823.

[2] S.T. Navale (2014). Facile method of preparation of PbS films for NO_2 detection. RSC Advances,**5**: 6518-6527.

[3] Mustafa K. A. Mohammed (2020) Studying the Structural, Morphological, Optical, and Electrical Properties of CdS/PbS Thin Films for Photovoltaic applications. Plasmonics, 15:1989–1996.

[4] Fatma Göde (2018). Synthesis and characterization of CdS window layers for PbS thin film solar cells. Materials Science in Semiconductor Processing, 90: 92-100.

[5] S. Kaci (2014). Preparation of nanostructured PbS thin films as sensing element for NO2 gas. Applied Surface Science, 305: 740-746.

[6] Ravikant (2019). template free synthesis of PbS nanoparticle sol-gel fecile method under IR radiation in room temperature. Applied Innovative reserch,1:101-105.

[7] Nasser Sad Al Din (2016). Structural and optical studied of nano structured lead sulfide thin films prepared by the chemical bath deposition technique. American Institute of physics, 1758(1).

[8] S. Seghaier (2006) Structural and optical properties of PbS thin films deposited by chemical bath deposition. Materials Chemistry and Physics, 97(1):71-80.

[9] Arzu Ekinc (2019) Chemical bath deposition of Co-doped PbS thin flms for solar cell application. Journal of Materials Science: Materials in Electronics,31**:**1210–1215.

[10] C. Rajashree (2015). Properties of Cd doped PbS thin films: doping concentration effect. Surface Engineering,31(4):316-321.

[11] Hossein Beygi (2019). Air exposure oxidation and photooxidation of solution-phase treated PbS quantum dot thin films and solar cells. Solar Energy Materials and Solar Cells, 203:110163.

[12] Ersin Yücel (2017). Fabrication and characterization of Sr-doped PbS thin films grown by CBD. Ceramics International, 43(1): 407-413.

[13] L S Chongad (2016). Synthesis of Lead Sulfide Nanoparticles by Chemical Precipitation Method. Journal of Physics, 755: 012032.

[14] Murat Alanyalıoglu (2009). Preparation of PbS thin films: A new electrochemical route for underpotential deposition. Electrochimica Acta, 54(26): 6554-6559.

[15] B Thangaraju (2000). Spray pyrolytically deposited PbS thin films.Semiconductor science and technology, **15**: 849.

[16] E. G ¨uneri (2015). Influence of grain size on structural and optic properties of PbS thin films produced by SILAR method. Thin solid film, 589: 578-583

[17] Sushil Kumar (2002). Characterization of vacuum evaporated PbS thin films. Physica B, 325: 8–16:

[18] M.S. Bhadane (2020) A post annealing effect on SrF2 nano particles: Structural, morphological, functional and dosimetric properties. Journal of Alloys and Compounds, 846: 156343