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Lead Sulfide(Pbs) Thin Film with Different Thiourea Concentrations

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ABSTRACT

In the present investigation PbS thin films were deposited on glass substrate with various thiourea concentration from 0.1 M to 0.3 M by chemical bath deposition method. The structural investigation was made with XRD patterns. With increasing thiourea concentration crystallites along (111) orientation is increased than (002) orientation. The average crystallite size was calculated using the Debye-Scherer's formula and it found that the value is increasing with increasing thiourea concentration. Surface morphological studies were carried out with Atomic Force Microscope. Surface modifications with various thiourea concentration was studied. Optical properties of the films were studied with UV-Vis Spectrophotometer and it is found that the films are having direct optical transition. Bandgap was calculated using the Tauc plot.

1. Introduction

Lead sulfide (PbS) is an IV-VI group of semiconductor having cubic crystal structure and direct narrow gap semiconductor material with an approximate energy band gap of 0.420 eV at 300 K and a relatively large excitation Bohr radius of 18 nm. PbS exhibit strong quantum size effects below excitonic Bohr radius of 18 nm, and hence energy band gap (Eg) of its nanocrystals can be tuned to anywhere between 0.41 (bulk) to 4 eV. These two properties make PbS films very suitable for infrared detection and solar cell applications. It is a material that has also been used in many fields such as photography, Pb^{2+} ion selective sensors, solar absorption etc.

Many research groups have shown a great interest in the development and study of PbS by various deposition processes. Chemical bath deposition (CBD) is attracting considerable attention as it does not require sophisticated instrumentation and it is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films. CBD prepared PbS thin films are reported to have a cubic centered structure with a preferential orientation of (200) perpendicular in direction to the plane of the substrate as well as being amorphous with lower spectral reflectance and transmittance [below 40%] in the wavelength range of 300 – 1800 nm [1]. Since the AFM analysis done by Seghaier, et al. (2006) showed a mixture of both PbS quantum dots and voids in their structure while that by Popa et al. (2006) reported an absorption band in the infrared range (1250 - 2400 nm) of 1.23 eV – 1.28 eV from absorption measurements and a band gap of between 0.93 eV – 1.0 eV from photocurrent measurement. It suggested that PbS thin films can be optimized and provide a good absorber material for both infrared and visible light spectrum [2].

CBD is a convenient and low cost technique for producing large area of semiconducting thin films. The basic principles underlying the chemical bath deposition of semiconductor thin films and early research work in this area is reviewed by Chopra et al. [3] which has inspired many researchers to initiate work in this area. The subsequent progress in this area is reported by Lokhande [4]. Since this is a low temperature process, this avoids oxidation and corrosion of the substrate. These are slow processes, which facilitate better orientation of crystallites with improved grain structure. The physical properties of chemical deposition of PbS films are dependent upon the growth parameters such as temperature, relative concentrations of various reactants in the solution, pH value and the type of substrate used. In addition, the growth processes in CBD method can be modified if the films are grown under the influence of external agents, for example the presence of magnetic fields [5]. For preparing PbS thin films Lead nitrate and thiourea has been used as Lead and sulfur sources respectively.

2. Experimental Methods

2.1 Preparation of PbS Thin Films

2.1.1 Substrate Cleaning

The PbS thin films were deposited on glass substrate by using CBD method. Before coating, the substrate should be cleaned well, as some impurities might be present in it. The glass slides were cleaned using concentrated Nitric acid, by dipping in it for 15 minutes. The nitric acid cleans the glass slides by doing a mild etching on the surface of the substrates. Then the substrates were washed with soap solution and finally rinsing in deionized water**.** The cleaned substrate is kept in ultrasonic bath for 20 min. Finally the substrate is cleaned by acetone solution [6].

2.2 Deposition of PbS Thin Films

Lead sulfide thin films were deposited on the glass substrate by chemical bath deposition method. Lead nitrate was used in the chemical bath as the source of lead, while thiourea as source for sulphur. PbS had been grown by the reaction between lead ions formed from the lead source and sulphur ions from thiourea. In this work, sodium hydroxide was used as a complexing agent. In the present work the bath solution were prepared from solutions of 0.17 M lead nitrate, 0.1 M thiourea, 0.57 M sodium hydroxide, to which 25 mL of distilled water was added. The overall bath solution was 50 mL. when the sodium hydroxide solution was added to the lead nitrate solution, there was some precipitation occurred. In order to avoid precipitate excess amount of sodium hydroxide solution was added drop by drop in to bath solution [1].

$$\mathrm{Pb\,(NO_3)_2 + 2NaOH \rightarrow Pb\,(OH)_2 + 2NaNO_3}$$
$$\mathrm{Pb\,(OH)_2 + 4NaOH \rightarrow NaPb\,(OH)_6}$$
$$\mathrm{NaPb\,(OH)_6 \rightarrow 4Na + + HPbO_2 + 3\,OH^- + H_2O}$$

Then Sulphur solution was mixed in bath solution and 25 mL of distilled water was added. The reaction process for forming lead sulphide films is considered as follows,

$$\mathrm{SC\,(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^-}$$
$$\mathrm{HPbO_2^- + SH^- \rightarrow PbS + 2\,OH^-}$$

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After 20 min, the bath solution was turned dark gray colour. Then cleaned substrate was vertically immersed into the solution. The beaker with the reactive solution was immersed in water heating bath circulator placed on heating magnetic agitator and was maintained at room temperature. The resulting films were homogeneous, well adhered to the substrate with darker surface like mirror was obtained.

2.3 Deposition Mechanism of PbS Thin Film

The deposition of the films from a solution involves a nucleation phase in which an initial layer of $Pb(OH)_2$ formed on the glass substrate is chemically converted into PbS by the reaction with S^{2-} ions available in the bath from the hydrolysis of thiourea. The presence of $Pb(OH)_2$ in the as-prepared bath is very vital for the deposition of PbS thin films. However, too much of a turbidity would lead to the incorporation of $Pb(OH)_2$in the films for deposition of longer duration [7]. The deposition rate at a constant temperature should be affected mainly by the concentration of thiourea and NaOH. Also, the quantity of thiourea predominantly affects duration of the deposition, while lower concentrations of thiourea give lower growth rates and longer incubation times. The deposition of the PbSfilms was done at the room temperature. The advantage of the low temperature used is that during the growth process there is a small possibility for the diffusion of the constituents of the depositing film into the substrate. After the deposition, the slides were removed from the chemical bath after different dipping times, rinsed with distilled water, dried and placed into a desiccator. A mirror-like surface was obtained (Table 1).

Table 1 List of the samples prepared

Sample	Pb:S:NaOH (volume ratio)	Tu^{2-}(M)	Deposition time (min)	Temperature (°C)
PbS	1:1:3	0.10	90	28 °C
PbS	1:1:3	0.17	90	28 °C
PbS	1:1:3	0.20	90	28 °C
PbS	1:1:3	0.25	90	28 °C
PbS	1:1:3	0.30	90	28 °C

3. Results and Discussion

3.1 Structural Properties

In the present investigation PbS thin films were deposited on glass substrate with various thiourea concentration from 0.1 M to 0.3 M by chemical bath deposition method. The structural investigation was made with XRD patterns. The powder X-ray diffraction pattern has been recorded between 20 to 80 with Brucker X-ray diffractometer using CuKα radiation at step size of 2θ = 0.02°. From the Fig. 1a, the XRD pattern, peak intensities were observed and matched with the JCPDS standards (JCPDS # 050592) and the peaks were indexed. The films were found to be polycrystalline behaviour. The maximum peak of the XRD pattern corresponded to the theoretical pattern of JCPDS data. Fig. 1a shown the XRD pattern of PbS thin films prepared by various thiourea concentration. The narrow peaks show that the material has good crystallinity preferentially oriented along the (2 0 0) direction which is perpendicular to the substrate and which intensity depends on thiourea concentrations. The XRD patterns of the as-prepared PbS thin films revealed that the synthesized thin films have face center cubic structure (*Fm*3*m*) [8]. The conditions for the FCC lattice: (i) h,k,l all are even or odd for the presence of reflection, (ii) h,k,l mixed even and odd for the absence of reflections and iii) $h^2+k^2+l^2$ = 3, 4, 8, 11, 23, 16, 19, 20, 24, 27, 32 for the presence of reflections, have been verified for all reflections between 2θ = 20° to 80°. The intensity and positions of the diffraction pattern match with the characteristic pattern of parent compound PbS which gives several prominent reflections between 2θ = 20° to 80° [3]. The average grain size was calculated by using Debye-Scherer's formula

$$D = (0.9\lambda/\beta COS\theta)$$

where *D* is the grain size, *β* is the FWHM of the diffraction peak, *θ* is the Bragg diffracting angle, *λ* is the wave length of X-rays and *d* is the inter planar spacing. With increasing thiourea concentration crystallites along (111) orientation is increased than (002) orientation. The average crystallite size was shown in Figure with thiourea concentration. The structural parameters of PbS is calculated from the XRD profile. Fig. 1b illustrates the full width half maximum (FWHM) vs *hkl*. Fig. 1c depicts the interplanar distance of PbS. The average crystalline size of the deposition film is shown in Fig. 1d with respect to the thiourea concentration. Seghaier et al. were reported that the thiourea concentration over and above 0.10 M, the thickness of PbS film reduced due to the poor crystallization [1]. But deposition time extended to 90 min, Fig. 1a showed good crystalline PbS film. For 0.10 M thiourea concentration, ion by ion deposition mechanism was take place to 90 min at 28 °C, crystallite size is 38.42 nm. While the crystallite size increased when thiourea concentration of 0.17 M and 0.25 M, due to PbS nucleation go on in a long time. The 0.20 M and 0.30 M thiourea concentration, PbS nucleation go off in a very short time and moreover, growth can occur without further nucleation of PbS, so that crystallite size is reduced. Figs. 1a and b shows that the FWHM of 0.25 M thiourea concentration of synthesized PbS have less as compared others and previous one have bigger sized crystalline, that is 81.18 nm as compared later and it is illustrate in Fig. 1d. Tables 2-4 show that structural parameters of PbS thin films for different thiourea concentrations from the Rietveld refinement.

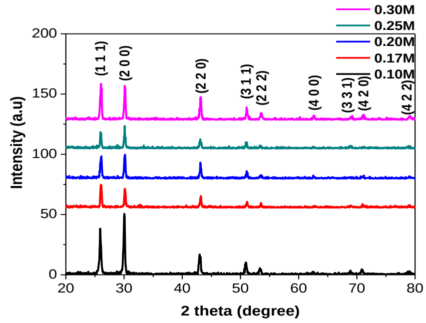

Fig. 1a The XRD pattern of PbS films for different thiourea concentrations

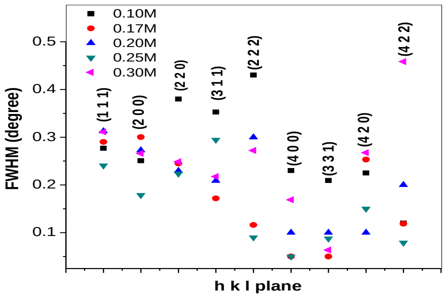

Fig. 1b FWHM of PbS films for different thiourea concentrations

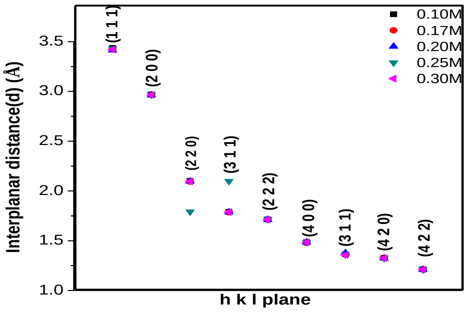

Fig. 1c Interplanar distance of PbS films for different thiourea concentrations

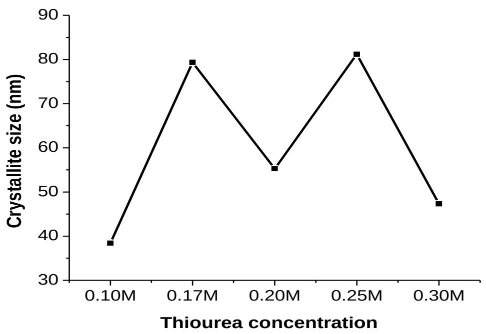

Fig. 1d Crystallite size of PbS films for different thiourea concentrations

Table 2 Structural parameters of PbS films for different thiourea concentrations from the Rietveld refinement

Parameters	0.10 M	0.17 M	0.20 M	0.25 M	0.30 M
a (Å)	5.94187	5.92564	5.93635	5.921	5.93091
Cell Volume (Å)	209.7821	208.0684	209.1988	207.58	208.6244
R factor	0.00084	0.00144	0.00144	0.0016	0.00132
Average D (nm)	38.41	79.36	55.29	81.18	47.32

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AFM images (2D and 3D) of PbS thin films for various thiourea concentrations is shown in the Fig. 2. At a lower thiourea concentration, different shapes of grains such as square, hexagonal and spherical are observed on the surface (Fig. 2). While increasing thiourea concentration, triangular shaped grains are observed uniformly throughout the surface. There will be a grains with number of planes are observed especially from the PbS film for the thiourea concentration of 0.25 M and 0.30 M. From the XRD pattern it is evidenced that with increasing thiourea concentration, the crystallites orientation along (111) is enhanced and the planes observed in the AFM images may have (111) orientation of crystallites. Even though the structure of PbS is face centered cubic, triangular shape of grains are predominantly observed here and earlier reports also [9, 10]. This can be clearly explained with observation of AFM images of Fig. 2 that when the cubes were bonded at different orientation which leads to the triangular shaped morphology on the surface.

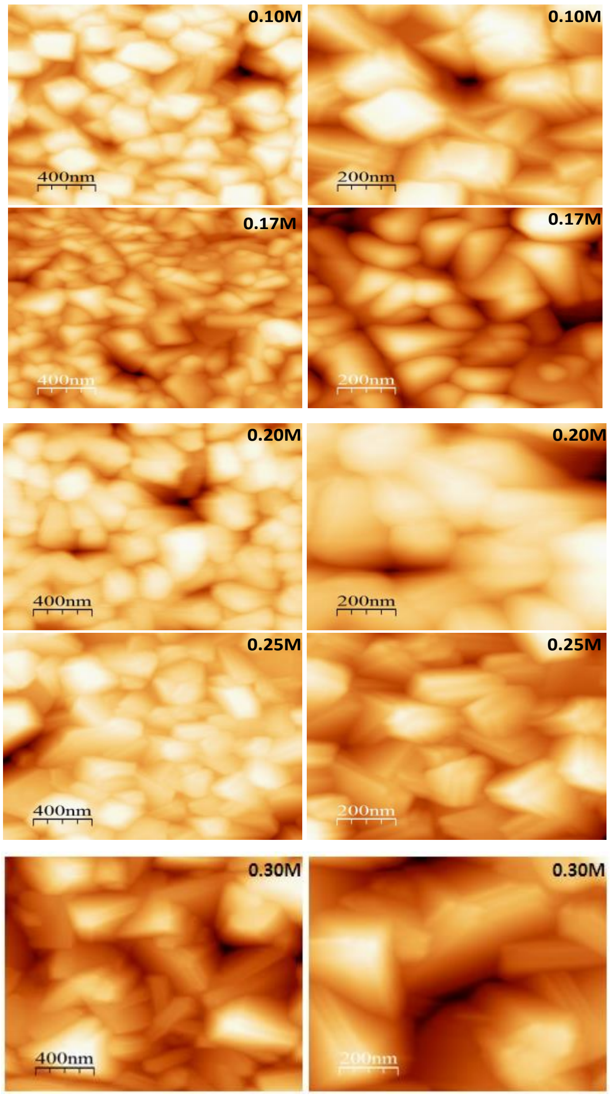


Fig. 2 AFM Images of PbS films for different thiourea concentrations

3.2 Surface Morphological Properties

Microstructure of the PbS has been studied by Field Emission Scanning Electron Microscope is shown in Fig. 3. It shows the particle with aggregation and irregular surface. The sizes of the particles are few hundred nanometers in range with various dimensions. The shape of the particle is uniform and it looks like cube, triangle and hexagonal. The microstructure of the thin film sample shows reduction in the agglomeration. The formed particles are clearly visible cube shape. Fig. 2 illustrates, particles are composed to form cluster and it was observed as sphere like morphology with different size shows the morphological analysis. The FESEM picture revealed that the PbS thin film is agglomerated particles of various sizes with rough surface. The particles grains on the surfaces suggesting that they were formed through fusion of the much smaller particles.

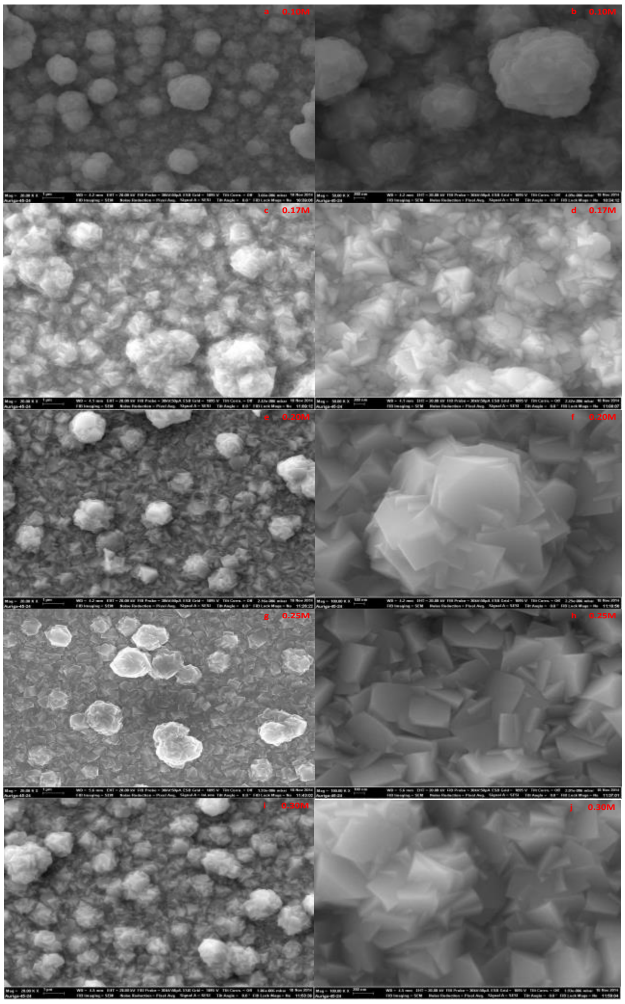


Fig. 3 FESEM images of PbS films for different thiourea concentrations

3.3 Raman Studies

PbS thin films are subjected to study Raman scatter at room temperature (300 K) using the Ar - ion laser with excitation wavelength of 632.9 nm. The existence of cubic phase in PbS was analysed with Raman spectrum. From the group theory analysis cubic phase PbS belongs to the space group of $Fm3m$. The expected optical mode T_{1u} is to be infrared active while other fundamental modes are Raman inactive. Whereas from group theory calculation, the Raman active first overtone modes are satisfied the combination rules of $T_{1u} \times T_{1u} = A_{1g} + E_g + T_{1g} + T_{2g}$[11]. Fig. 4 illustrates the 1LO and 2LO (longitudinal optic) mode observed at 202 cm^{-1} and 453 cm^{-1} respectively by the elastic neutron scattering. The wavenumber around 193.5 cm^{-1} is revealed by the surface mode, exciton-phonon coupling Raman scattering.

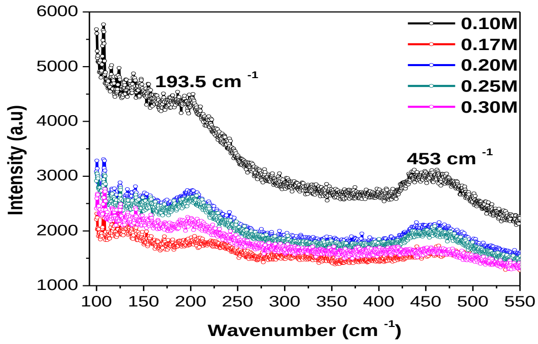


Fig. 4 Raman spectra of PbS thin film for different thiourea concentration

3.4 Optical Properties

The absorption and transmission spectra of PbS thin films recorded in the UV and visible range are given in Fig. 5. Moreover, the Fig. 5a shows that the absorption peak is seemed to be smaller than expected, which is due to the thickness of film is less than 100 nm. Since the lead chalcogenides have high dielectric constants (therefore high refractive indices and high reflection), masking of weak or even moderate absorption by reflection is probable [12]. PbS thin film was observed to exhibit a high transmittance in the IR region. The spectra depict that the transmittance of samples in IR region is around 20 to 45%.

Absorption edge shifted towards higher wavelength region when the thiourea concentration is increased. The absorption coefficient has been calculated using the following relationship [13].

$$\alpha = [-\ln (T)\, h\upsilon]^2$$

where, α is the absorption coefficient; T is the transmittance

In order to know the transition in the fundamental absorption is whether direct or indirect, both linear dependence study of plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ against hν made. It is found that PbS thin films prepared for different thiourea concentration possess direct optical transition. Bandgap have been calculated by extrapolating the linear portion of the graph as shown in Fig. 6, to the hν axis. This band gap causes a crystallite size and this is correlated with the XRD and AFM results.

Table 3 Bragg's angle, interplanar distance, crystallite size of PbS films for different thiourea concentrations

	0.10 M				0.17 M				0.20 M				0.25 M				0.30 M			
h k l	2θ	d(A)	FWHM	D(nm)	2θ	d(A)	FWHM	D (nm)	2θ	d(A)	FWHM	D(nm)	2θ	d(A)	FWHM	D nm	2θ	d(A)	FWHM	D (nm)
1 1 1	25.90	3.4363	0.2769	29.4	26.02	3.421	0.2901	27.8	26.08	3.4138	0.3128	25.8	25.95	3.4303	0.2407	33.5	26.03	3.4199	0.3109	25.9
2 0 0	30.05	2.9709	0.2506	32.8	30.12	2.9641	0.3002	27.1	30.14	2.9624	0.2728	29.8	30.10	2.9664	0.1786	45.5	30.11	2.9648	0.266	30.6
2 2 0	42.98	2.1023	0.3799	22.5	43.19	2.0928	0.2449	34.5	43.11	2.0962	0.2294	36.8	50.95	1.7908	0.2236	38.9	43.15	2.0948	0.2486	34.0
3 1 1	50.91	1.7920	0.3527	24.9	51.13	1.785	0.1719	50.7	51.06	1.7872	0.2089	41.7	43.1	2.0971	0.2944	28.7	51.06	1.7871	0.2175	40.0
2 2 2	53.34	1.7159	0.43	20.7	53.51	1.7109	0.1161	75.8	53.52	1.7106	0.3	29.3	53.39	1.7144	0.09	97.7	53.50	1.7111	0.2722	32.3
4 0 0	62.49	1.4850	0.23	40.4	62.8	1.4784	0.05	184.0	62.49	1.4849	0.1	91.9	62.5	1.4848	0.05	184.0	62.56	1.4835	0.1688	54.5
3 3 1	68.90	1.3616	0.2094	46.0	68.9	1.3617	0.05	191.0	67.96	1.3781	0.1	94.7	68.95	1.3608	0.0875	109.0	69.19	1.3565	0.0635	150
4 2 0	70.84	1.3290	0.225	43.3	70.96	1.3271	0.2531	38.1	71.20	1.3231	0.1	96.6	71.25	1.3223	0.15	64.4	71.14	1.3241	0.2675	36.1
4 2 2	78.76	1.2140	0.12	85.6	79.06	1.2101	0.1188	85.7	79.00	1.2109	0.2	50.9	78.99	1.2110	0.0788	129.0	79.07	1.2100	0.4583	22.2

Table 4 Structural parameters of PbS films for different thiourea concentrations from the Rietveld refinement

h	k	l	0.10 M			0.17 M			0.20 M			0.25 M			0.30 M		
			TH(OBS)	TH(CALC)	DIFF.	TH(OBS)	TH(CALC)	DIFF.	TH(OBS)	TH(CALC)	DIFF.	TH(OBS)	TH(CALC)	DIFF.	TH(OBS)	TH(CALC)	DIFF.
1	1	1	12.95373	12.97594	-0.0151	13.01042	13.01208	0.00408	13.04063	12.98819	0.00961	12.9765	13.02246	0.01127	13.01685	13.00031	-0.01218
2	0	0	15.02697	15.02726	0.00682	15.0625	15.06937	-0.00113	15.07143	15.04154	-0.01293	15.05028	15.08146	0.02604	15.05884	15.05566	-0.02553
2	2	0	21.49375	21.51071	-0.00986	21.59583	21.57255	0.02902	21.55909	21.53168	-0.01541	21.55	21.59031	0.01692	21.575	21.55241	-0.00613
3	1	1	25.45724	25.46533	-0.00099	25.56528	25.54005	0.03096	25.53092	25.49066	-0.00256	25.47656	25.56151	-0.02772	25.53224	25.51572	-0.01219
2	2	2	26.67292	26.6849	-0.00488	26.7575	26.76377	-0.00053	26.7625	26.71164	0.00804	26.69861	26.78642	-0.03058	26.75357	26.73809	-0.01323
4	0	0	31.24583	31.23551	0.01742	31.4	31.33069	0.07505	31.24688	31.26778	-0.06372	31.25	31.35803	-0.0508	31.28036	31.29969	-0.04805
3	3	1	34.45288	34.40816	0.05183	34.45	34.51566	-0.05992	0	0	0	34.475	34.54655	-0.01433	34.59844	34.48064	0.08908
4	2	0	35.42159	35.43397	-0.00528	35.48068	35.54567	-0.05925	35.60312	35.47184	0.08847	35.6275	35.57776	0.10697	35.57188	35.50928	0.03388
4	2	2	39.38036	39.42741	-0.03995	39.5325	39.5565	-0.01826	39.5025	39.47116	-0.01148	39.49861	39.5936	-0.03776	39.5375	39.51444	-0.00565

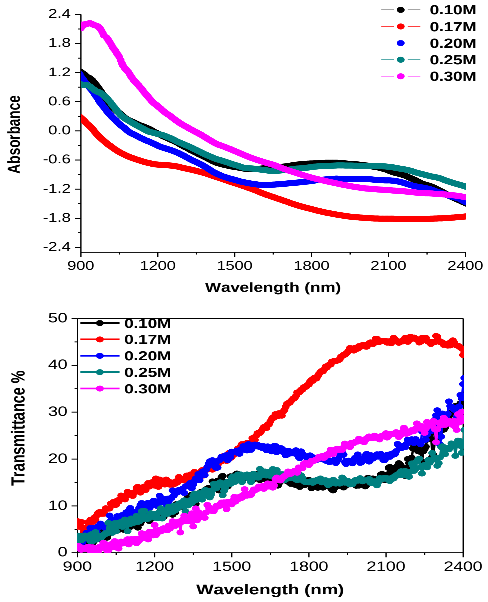
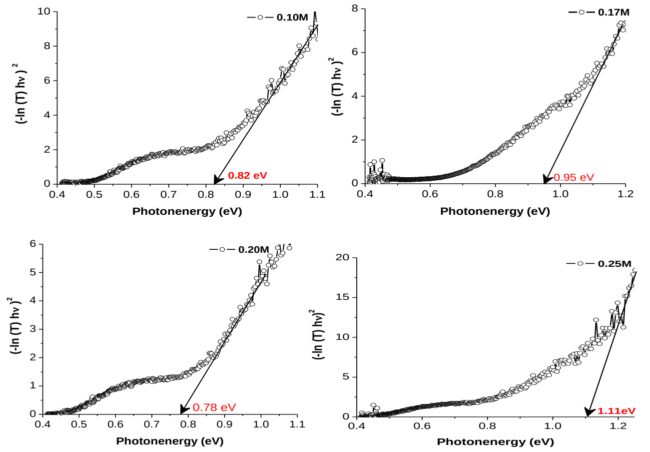


Fig. 5 UV-Vis-IR transmission spectra of PbS thin film for different thiourea concentration



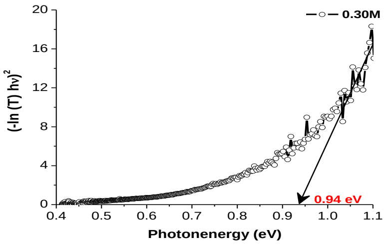


Fig. 6 Tauc extrapolation graph of PbS thin film for a) 0.10 M, b) 0.17 M, c) 0.20 M d) 0.25 M and e) 0.30 M thiourea concentration

4. Conclusion

PbS thin films prepared by low cost chemical bath deposition technique is technologically important in optoelectronic devices and electrodes in solar cells. In order to ensure the quality of material, various studies are performed with different parameters. In this focus we have studied the properties of PbS thin films with different thiourea concentration. In our present research, with increasing thiourea concentration in the preparation of PbS thin films following results are obtained i) crystallites on (111) orientation is increased and the unit cell density is increased, ii) improved surface morphology, iii) decreases in bandgap and iv) decreases in resistivity. These results will be helpful in improving the properties and fabricating the devices.

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