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EFFECT OF DEPOSITION PARAMETERS ON GROWTH AND CHARACTERIZATION OF CHEMICALLY DEPOSITED $Cd_{1-X}Pb_XS$ THIN FILMS

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A Simple and cost effective chemical bath deposition process has been employed for the preparation of $Cd_{1-x}Pb_xS$ (x = 0.00, 0.20, 0.40, 0.60, 0.80, 1.00) thin films. Cadmium sulphate, lead sulphate and thiourea were used as the basic source materials. The effect of various preparative parameters such as bath composition, pH of the reaction solution, deposition temperature and time, speed of the substrate rotation and the complexing agent on growth process is studied and these parameters are optimized for good quality films. The colour of the 'as-deposited' thin films has changed from orange yellow to black as the composition parameter x changed from 0 to 1. The film thickness is found to be increased with increasing the composition parameter x from 0 to 1. The X-ray diffraction (XRD) studies revealed that films are polycrystalline in nature and exhibit both cubic and hexagonal structure for pure CdS but only cubic phases for pure PbS film. The energy dispersive analysis by X-rays (EDAX) studies revealed that films are cadmium rich. The energy band gap is decreased from 2.47 eV to 0.49 eV as composition parameter 'x' is increased from 0 to 1.

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Keywords: Chemical bath deposition, $Cd_{1-X}Pb_XS$ Thin films, XRD. EDAX

1. Introduction

The ternary semiconductor thin films are considered to be an important technological material due to its prime applications in various optical and electronic devices. The II-VI and IV-VI group compound materials having specific physical properties like high efficiency, high optical absorbance and direct band gap, are considered to be potential materials in respect for a wide spectrum of optoelectronic applications such as photo detectors, photovoltaic devices, photo-electrochemical cells [1-4], lasers, IR devices, solar control coatings, [5-6], solar cells [7]. These materials can be deposited in thin film form by various methods, such as electro-deposition [8-9], spray pyrolysis [10], vacuum deposition [11] and chemical bath deposition [12-18]. Among them the chemical bath deposition method is very simple, convenient for large area deposition on substrates of different materials, size and shape and it is inexpensive. Especially, one of the attractive features of the chemical bath deposition process is the ease with the alloys can be generated without the use of any sophisticated instrumentation and process control [19].

The objective of present work is to optimize various preparative parameters to synthesize the ternary $Cd_{1-x}Pb_xS$ thin films by chemical bath deposition method to understand growth mechanism and reaction kinetics. Further, films will be characterized through XRD, EDAX and spectroscopic techniques to know thin film structure and composition in order to make them suitable candidate for various optoelectronic and nanodevice application.

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2. Experimental details

2.1 Substrate preparation

The microscopic glass substrates of dimensions 75 X 25 X 1.3 mm (Blue Labels Scientific Pvt. Ltd. Mumbai) were cleaned with detergent several times and then boiled in chromic acid (2M) for 30 minutes. Then these substrates were washed with double distilled water and stored in dark desiccators and then used for the deposition.

2.1.1 Deposition of pure CdS film

Pure CdS thin film has been deposited onto well processed glass substrate from a reaction mixture consisting of equimolar cadmium sulphate and thiourea. A 10 ml cadmium sulphate solution was taken in a reaction container and complexed with an appropriate quantity of triethanolamine to obtain a stable Cd-TEA complex. Liquid ammonia and sodium hydroxide were added to adjust pH of the solution. Then 10 ml thiourea was added to reaction mixture. The reaction mixture was kept in oil bath at a suitable temperature in which thoroughly cleaned glass substrates were positioned vertically to specially designed substrate holder kept it rotated. For good quality CdS film the various preparative parameters like speed of rotation, deposition time and temperature of bath and pH of the reaction mixture have been optimized.

2.1.2 Deposition of pure PbS film

Similar procedure was employed to deposit PbS thin films. However, instead of cadmium sulphate, lead sulphate was used.

2.1.3 Deposition of $Cd1_{-X}Pb_XS$ films

For $Cd_{1-x}Pb_xS$ composite films the volume stoichiometric quantities of cadmium sulphate and lead sulphate were added into the reaction container to obtain the value of composition parameter x from 0 to 1. An appropriate quantity of triethanolamine and sodium hydroxide were added to form stable complex. Then liquid ammonia was added into the reaction solution. The rest of the procedure was same as that for the CdS.

2.2 Characterization technique

The thickness of $Cd_{1-x}Pb_xS$ thin film was estimated by using the gravimetric weight difference method. The X-ray diffractograms were recorded by using a Philips PW-3710 X-ray diffractometer (XRD) with Cu k_α line ($\lambda = 1.54056A^0$) in the 2θ range from 20^0 to 80^0. The compositions of samples were determined by energy dispersive x-ray spectroscopy (EDAX) using JEOL JSM 5600. The optical studies were carried out using UV-VIS-IR spectrophotometer (Cary-5000) in the 350-3200 nm wavelength range.

3. Result and discussion

3.1 Film kinetics:

3.1.1 CdS film kinetics

The rate of CdS thin film growth is mostly dependent on the rate of release of Cd^{2+} and S^{2-} ions from the complex state which condense on an ion by ion basis on the glass substrate. Generally, the metal chalcogenides MX (where X = S, Se, Te) is formed when the ionic product (IP) of M^{2+} and X^{2-} exceeds its solubility product (SP). The ratio IP/SP=S gives the super saturation of the ions over MX. S can be changed by changing appropriate initial concentrations of

the reactants. When S>1, the ions combine on the substrate and in the solution to form MX nuclei which they grow with time to give a film and precipitate. So, the concentration of Cd^{2+} and S^{2-} ions have to be controlled very carefully during the film growth [20]. This can be achieved by using a high stability complexant and other parameters such as pH of the reaction mixture, deposition time and temperature and speed of substrate rotation in reaction bath and initial concentrations of ions. The mechanism of film formation can be understood from the following reaction.

$$Cd\,[N(CH_2CH_2OH)_3]^{2+} + (NH_2)_2CS + 2OH^- \text{ ---------> } CdS + \text{ Waste product.}$$

3.1.2 PbS film Kinetics

The formation of PbS film depends on the rate of release of Pb^{2+} and S^{2-} ions from the bound state. The film grew by a nucleation process involving an energetic-atomistic condensation of the ions on the substrate to form PbS nuclei, which then grew in size by adsorbing more and more ions from the reaction bulk. The controlled rate of arrival of Pb^{2+} and S^{2-} ions on the substrate surface from the solution controls the rate of film formation and its growth rate.
The mechanism of film formation is

$$Pb\,[N(CH_2CH_2OH)_3]^{2+} + (NH_2)_2CS + 2OH^- \text{ ---------> } PbS + \text{ Waste product.}$$

3.1.3 $Cd_{1-X}Pb_XS$ film kinetics

Similarly the formation of CdPbS film depends on the rate of release of Cd^{2+}, Pb^{2+} and S^{2-} from the bound state. The fundamental chemical reaction is

$$[Cd(N(CH_2CH_2OH)_3)^{2+}]_{(1-X)} + [Pb(N(CH_2CH_2OH)_3)^{2+}]_X + (NH_2)_2CS + 2OH^- \text{ --------->}$$

$$Cd_{1-X}Pb_XS + \text{Waste product}$$

The color of the deposits changed from orange to black as the composition parameter x has increased from 0 to 1.

3.2 Effect of preparative parameters

3.2.1 Composition of reaction solution

The film growth can be affected by changing the composition parameter x of the reaction solution. The change in bath composition can alter the processes of homogeneous nucleation and heterogeneous nucleation and ultimately the growth of thin films [21]. The hydroxide species plays an important role in film formation and acts as nucleation centers on the substrates. The proper amount of hydroxy species in bath solution enhances the film growth and gives good quality film. The good quality CdPbS thin film is associated with supersaturated bath, cadmium and lead hydroxide species. If the bath contains low concentration of bath ingredients generally favors the nucleation in early stage. By many more trial and error method, 1 molar concentration has been optimized. Fig.1. Shows variation of film thickness with molar concentration.

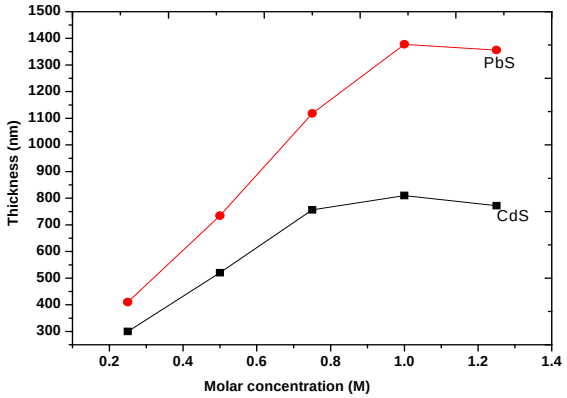

Fig.1. Variation of film thickness with molar concentration.

It is well known that the bath concentration plays an important role, when bath contains high concentration the films formed were thicker and for low concentration films too thin and non uniform and non homogeneous. This indicates that there is lack of required number of ionic species for better quality film. Above certain concentration when rate of reaction becomes high and precipitation also becomes important leading to lesser amount CdS/PbS on the substrate and hence lowers the thickness [22].

3.2.2 pH of the reaction solution.

For the growth of good quality thin films, the hydroxy ions in precursor solution is necessary [23]. The thin film formation depends on the pH of the reaction mixture and pH depends on OH ions. By the observation of Kaur et al. [24], the decomposition of chalcogen is stimulated by presence of solid phase such as Cadmium hydroxide and Lead hydroxide. At our experimental conditions it was found that good quality CdPbS thin films can be deposited at pH ranging between 9.5-11.5. At this condition the alkaline hydrolysis and sulpher source release S^{-2} ions. The reactivity of hydroxide ions with metal ions affects when pH of the solution decreased. The decrease in pH results porous, non-reflecting, powdery and weakly adhered thin films on the substrates. Increasing the pH value above 9.5 nonporous, uniform, smooth, tightly adherent and reflecting thin films obtained. At higher pH metal ion concentration will be lower and the reaction rate will be slow. With an increase in pH as the metal ion concentration decreases, the rate of film formation decreases [25]. So, throughout the experimental procedure of deposition pH value is maintained at 10.5 ± 0.1. Fig. 2. shows the variation of film thickness with pH.

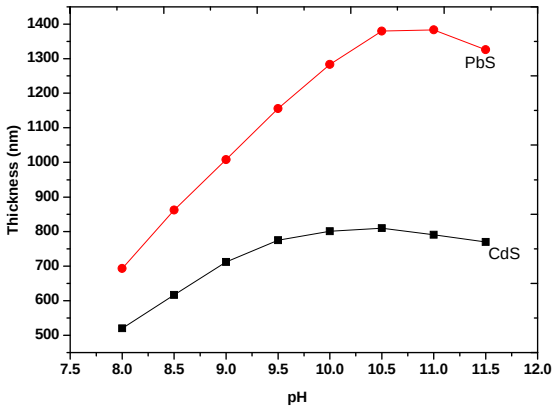

Fig.2. Variation of film thickness with pH.

3.2.3 Effect of deposition temperature and time

It was observed that at room temperature no film formation takes place. It may be due to at low temperature almost all the metal ions are in a complex-bound state, there may not be free ions for film formation. When temperature of bath container is increased to 80 ^{0}C good quality and adherent CdPbS films were deposited on glass substrates.

Fig. 3. shows the variation of film thickness with temperature. It has seen that the terminal layer thickness is increased with increase in temperature linearly up to 80 ^{0}C and above 80 ^{0}C it decreases. It is clear that at 80 ^{0}C, thermal energy is sufficient to make ions free from bound complex state which increases the rate of film formation. Above 80 ^{0}C temperature the reaction gave precipitation rather than film which settled down at the bottom of container, as a result layer thickness of CdPbS thin film was found to be decreased [25].

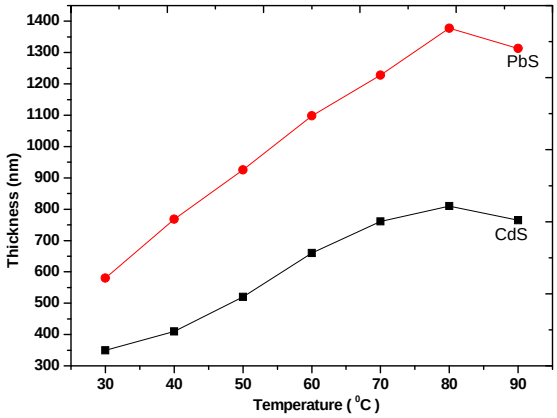

Fig.3. Variation of film thickness with temperature.

The film deposition time with respect to thickness was also studied. The deposition of thin of thin film for 30, 40, 50, 60, 70, 80, and 90 minutes were studied. The terminal thickness was measured after every 10 min. The CdPbS thin films were deposited at 60 min. It is observed that film growth is time-dependent and is initially quasi-linear, and after 60 minutes it saturates. It may be due to the fact that the volumetric ion concentration to surface substrate ratio decreases as time increases and finally results in a terminal layer thickness [25]. So in the present study CdPbS thin films have deposited for 60 min. time period. Fig.4. Shows the variation of film thickness as a function of time.

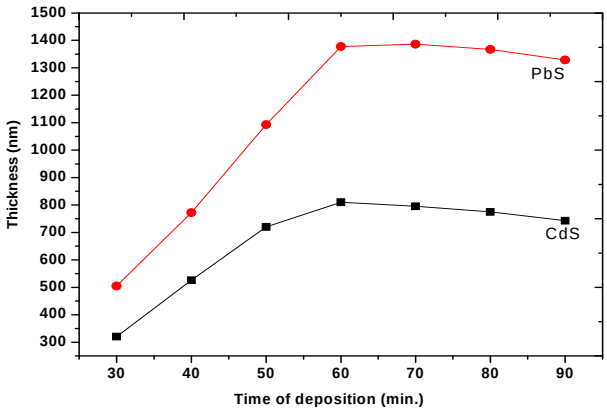

Fig.4. Variation of film thickness with deposition time.

3.2.4 Effect of speed of the substrate rotation

Speed of the substrate rotation is one of the important parameter in chemical bath deposition technique. It affects the film formation process. In case of CdPbS, the speed of substrate rotation is moderated to 65 rpm to obtain sufficient layer thickness and quality film. When the rotation speed is decreased, thick porous and non-sticky film was formed, while at a speed greater than 65 rpm very thin adherent, reflecting film deposition was found. Fig.5. shows variation of film thickness with speed of substrate rotation.

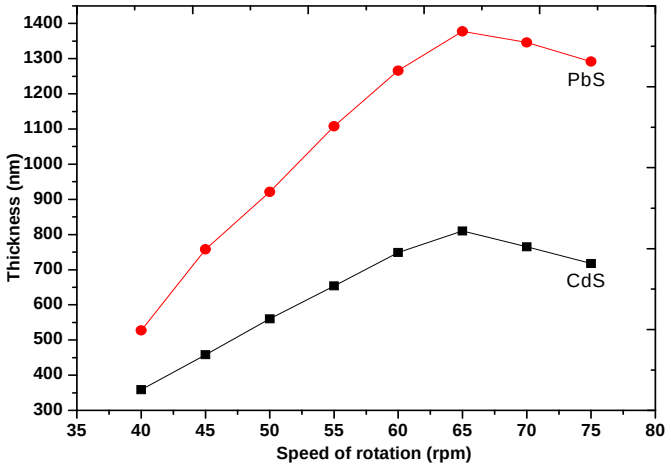

Fig.5. Variation of film thickness with speed of substrate rotation.

3.2.5 Role of complexing agent

The deposition of thin film on glass surface is an adsorption phenomenon. Film formation occurs by combination of released metal ions from complex metal ion source and chalcogen source. In the present study triethanolamine is used as the complexing agent. With the help of triethanolamine complexed metal ion can be made free in alkaline medium of pH value 10.5 ± 0.1. It helps to limit the hydrolysis of the metal ion and impart some stability to bath otherwise it undergoes rapid hydrolysis and precipitation. If less amount of triethanolamine is used fast precipitation occurs, when excess triethanolamine is used less number of ions are available for film formation, so thinner films formed [26]. In the present study pH of solution is optimized at 10.5 ± 0.1for good quality films. Fig.6. shows variation of film thickness with complexing agent and Fig.7. shows variation of film thickness with composition parameter x.

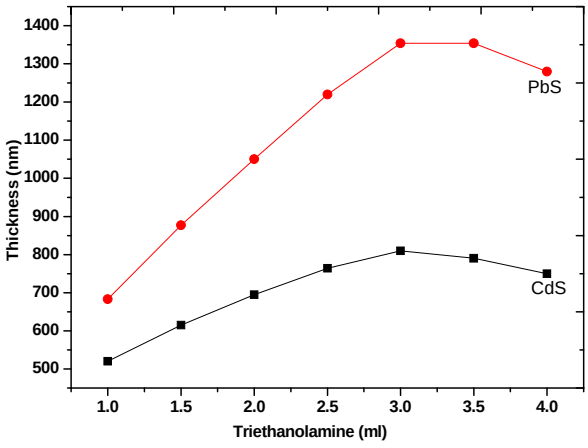

Fig.6. Variation of film thickness with complexing agent.

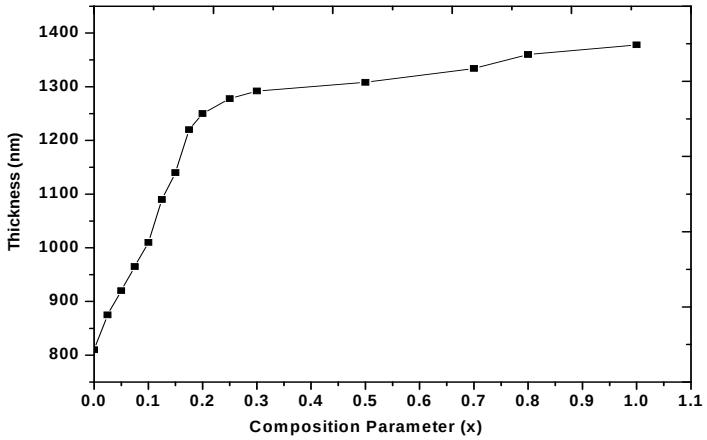

Fig.7. Variation of film thickness with composition parameter.

3.3 XRD analysis

The X-ray diffractograms of 'as-deposited' cadmium lead sulphide films prepared by chemical bath deposition is shown in Fig.8. The presence of large number of peaks indicates that the films are polycrystalline in nature with cubic and hexagonal structure [27] For CdS (x = 0), the prominent peaks corresponding to (111), (200), (220) and (311) planes of the material with cubic phases matched with standard JCPDS data card 80-0019, while peaks corresponding to (002), (111) and (110) planes are matched with standard JCPDS data card 80-0006 of CdS hexagonal crystal structure. For PbS (x = 1), the preferential orientation is along (111), (200), (220), (311), (222), (420), and (422) planes matched with standard JCPDS data card 05-0592. In the XRD pattern some other phases such as cubic CdO, CdO_2, tetragonal PbO and PbO_2 and elemental S, are observed.

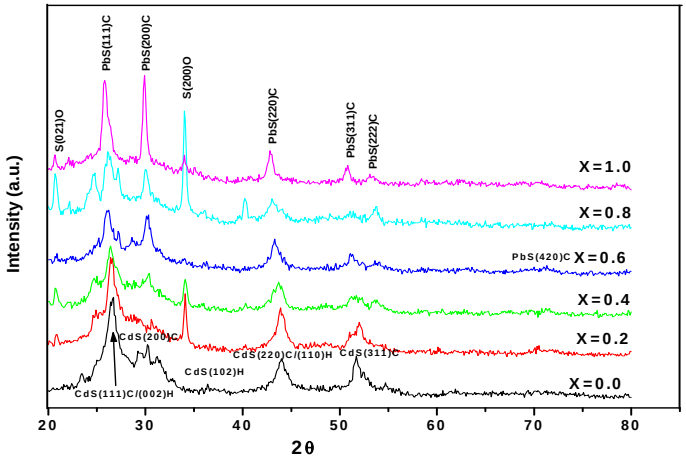

Fig.8. X-ray diffractograms of as deposited $Cd_{1-x}Pb_xS$ thin films.

The lattice parameters a and c for hexagonal phase and cubic phase were determined. For hexagonal structure, the lattice constant 'a' varies from 4.1035 A^0 to 4.1728 Å and 'c' form 6.6382 Å to 6.6947 Å .

The grain size was calculated by using Scherer's equation

$$D = 0.94 \lambda / \beta \cos\theta$$

Where λ is the wavelength of X-ray used, β is the full width at half maximum in radian, and θ is the Bragg's diffraction angle.

The average grain sizes are in the range 7.1 to 15.5 nm and listed in table 1.

Table 1. Some characteristic parameters and elemental composition of chemically deposited $Cd_{1-x}Pb_xS$ thin films.

Composition Parameter (x)	E_g (eV)	Grain size, D (nm)	Initial atomic percentage in bath solution of film (%)			Final atomic percentage in film by EDAX analysis (%)		
			Cd	Pb	S	Cd	Pb	S
0.00	2.47	7.1	50	00	50	57.45	00	42.54
0.02	2.04	15.5	40	10	50	46.05	12.34	41.61
0.04	1.64	10.6	30	20	50	34.16	23.87	41.97
0.06	1.22	9.2	20	30	50	27.89	32.23	40.88
0.08	0.85	8.1	10	40	50	---	---	---
1.00	0.49	7.5	00	50	50	00.00	60.95	39.05

3.4 EDAX analysis

Fig.9. Shows the EDAX pattern for representative $Cd_{0.4}Pb_{0.6}S$ thin film. The pattern confirms the presence of cadmium, lead and sulpher. The proportion of these elements measured as Cd = 27.89 %, Pb= 32.23 % and S= 40.88 %. The other EDAX data is given in table 1. The result indicates that the deposited films are non-stoichiometric in composition. EDAX analysis shows that the films are cadmium reach. It may be due to the fact that the reactivity of cadmium is more than sulpher ions [28]. The deviation in the composition can be adjusted by changing the volume or concentration or both of the individual ion sources in the reaction mixture.

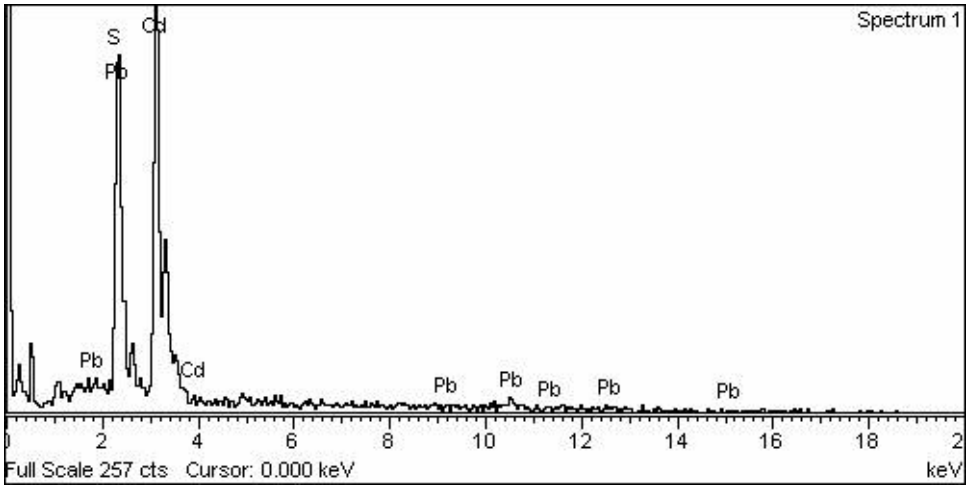

Fig.9. EDAX pattern of $Cd_{0.4}Pb_{0.6}S$ thin film.

3.4 Optical properties

The optical properties of 'as-deposited' $Cd_{1-x}Pb_xS$ thin films were measured by using UV-VIS-NIR spectrophotometer at room temperature in the wavelength range 350-3200 nm. The

optical studies revealed that the films are highly absorptive with a direct type of transition. The optical band gap (E_g) is determined using the classical relation

$$(\alpha h\upsilon) = A\,(h\upsilon - E_g)^{1/2}$$

Where 'A' is a constant and 'hυ' is the radiation energy. Fig. 10. shows the plot of $(\alpha h\upsilon)^2$ vs hυ for different composition. The linear nature of the plots at the absorption edge confirmed that $Cd_{1-x}Pb_xS$ is a semiconductor with a direct band gap. The optical band gap is varied from 2.47 eV (CdS) to 0.49 eV (PbS). The variation of band gap with the composition of x is shown in table 1. It is observed that small amount of Pb present in the films greatly affects the optical band gap of CdS. The band gap was observed to decrease with an increase in the concentration of Pb in the deposits. The nature of this variation in the band gap energy may be useful to design a suitable window material in fabrication of solar cells.

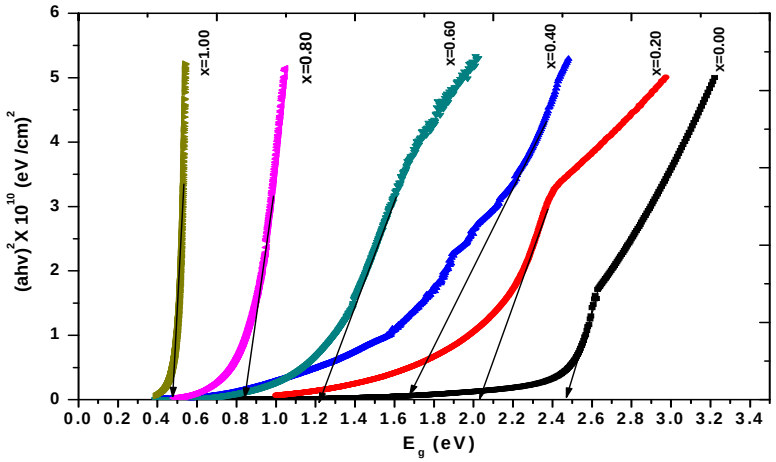

Fig.10. Plot of $(\alpha hv)^2$ vs hv for chemically deposited $Cd_{1-x}Pb_xS$ thin films.

4. Conclusions

From above study it is concluded that thin, uniform and adherent cadmium lead sulphide thin films with different composition parameter $0 \leq x \leq 1$ can be deposited successfully by simple chemical bath deposition technique. The effect of various preparative parameters such as composition of bath, pH of the reaction solution, deposition temperature, and deposition time, speed of substrate rotation and nature of complexing agent on growth process is studied. XRD studies reveal that the 'as deposited' thin films are polycrystalline in nature with cubic and hexagonal phases. EDAX spectra confirmed that the films are sulpher deficit. The optical band gap energy is evaluated for various compositions and it is found to decrease from 2.47 eV to 0.49 eV.

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