SYNTHESIS AND CHARACTERIZATION OF CHEMICALLY DEPOSITED Cd_{1-x}Pb_xS THIN FILMS

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A simple and inexpensive chemical bath deposition technique is employed for the deposition of $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films. Cadmium sulphate, lead sulphate and thiourea were used as the basic starting materials. Triethanolamine (TEA) was used as complexing agent. For good quality deposits the various preparative parameters such as deposition temperature, time, speed of substrate rotation and pH of the reaction mixture were optimized to 80 °C, 60 min., 65 rpm and 10.5±0.1 respectively. The 'as-grown' samples were characterized through structural, surface morphological, compositional, optical, electrical and thermoelectric studies. The colour of 'as-grown' samples went on changing from orange yellow to black with increase in composition parameter 'x' from 0 to 1. The thickness of the samples went on increasing with the composition parameter 'x'. The X-ray diffractograms of 'as-grown' samples exhibited polycrystalline nature with presence of cubic phases for CdS and PbS and hexagonal phase for CdS alone. The crystal size determined from XRD and SEM micrographs is observed to increase with 'x' up to 0.175 and later on it decreased. The energy dispersive analysis by X-rays (EDAX) revealed that films are cadmium rich. The optical study at room temperature revealed high coefficient of absorption (10^4 cm^{-1}) with a direct allowed type of transition with band gap energy decreasing continuously from 2.47 eV to 0.49 eV with varying composition parameter 'x'. The electrical resistivity measurements revealed semiconducting nature of the film and it is found that the resistivity of the film decreases with increase in 'x' up to 0.175 and further it increases up to x = 1. The n-type conduction was observed in film from TEP studies.

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1. Introduction

The fabrication of binary and ternary semiconductor materials in varying sizes and shapes is currently one of the fastest growing area of materials research due to their interesting applications in non-linear optics and opto-electronic devices [1-4]. Cadmium sulfide (CdS) is a II-VI group semiconductor with energy gap covering the visible spectral range, which is used in many applications such as visible light emitting diodes and lasers [5-6], photovoltaic and photo-conductive devices [7]. On the other hand PbS is a semiconductor material belonging to IV-VI group with a direct narrow band gap (0.41 eV) suitable for infrared detection applications [8-9]. It has also been used as photo resistance, laser diode, humidity and temperature sensors, decorative coatings and solar control coatings [10-13]. However, only a limited number of studies have been conducted on ternary II-IV-VI compounds. These materials have attracted a great deal of attention, both from the fundamental and applied point of view. These materials are used in optoelectronics, solar control coatings, gas and humidity sensors and photoelectrochemical solar cells [14-16].

Roger and Crocker carried out an extensive study of the electrical properties of $Pb_{1-x}Cd_xTe$ and $Pb_{1-x}Mg_xTe$ using bulk material [17]. Harman and coworkers reported that bulk crystals of $Pb_{1-x}Cd_xS$ could be prepared beyond the stable phase boundary limits by quenching [18].

Due to the optical, electrical and photoelectrical properties of $Cd_{1-x}Pb_xS$ is one of the promising material having large spectrum of applications in selective coatings for efficient photothermal conversion to obtain absorbance in the UV-VIS region and reflectance in IR region. These films can be used for controlled absorption and reflection of solar light [19-20].

Thin metal chalcogenide films can be obtained by chemical bath deposition (CBD) method [11, 20], spray pyrolysis [13], physical and electrochemical technique [21-23]. Among these methods, CBD is simple and inexpensive to obtain homogenous hard, adherent and transparent thin films, useful for large area industrial applications. The CBD technique involves the controlled precipitation, which offers many advantages over the CVD, MBE and spray pyrolysis. The important advantage of CBD with respect to other methods is that films can be deposited on different kinds, shapes and sizes of substrates [24-25].

In the present study, considering the advantages laid down by ternary compounds, the chemical bath deposition technique is used for the deposition of $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films. The growth, structural, surface morphological, compositional, optical and electrical properties have been studied over entire range of composition. The results obtained are discussed and compared

2. Experimental details

The Cd_{1-x}Pb_xS thin films with $0 \le x \le 1$ were deposited onto ultrasonically cleaned glass substrates by chemical bath deposition technique. For the deposition, equimolar solutions (1M, all AR grade) of cadmium sulphate, lead sulphate and thiourea (Thomas Baker made) were mixed in stoichiometric proportion. Triethanolamine was used as complexing agent. pH of the reaction mixture was adjusted by adding NaOH and liquid ammonia. The deposition was carried out in a beaker (250 ml) kept in uniformly heated programmable temperature controlled (DTC-201, Creative) oil bath. Well processed glass substrates were mounted vertically on a specially designed substrate holder and were rotated in reaction mixture to achieve uniform churning. Good quality samples were deposited at optimized temperature, time of deposition, speed of substrate rotation and pH at 80 $^{\circ}$ C, 60 min., 65 rpm, and 10.5±0.1 values respectively.

The thickness of 'as-grown' samples was measured by gravimetric weight-difference density method using sensitive microbalance. The structural properties of these film samples were studied using Philips PW-3710 X-ray diffractometer with Cuk_a line ($\lambda = 1.54056$ Å) in the 20 range from 20^o to 80^o. The film surface morphology and composition was investigated using scanning electron microscopy (SEM) and energy dispersive analysis by X-ray with JEOL-JSM 5600 scanning electron microscope respectively. The optical absorption studies were carried out using UV-VIS-IR spectrophotometer (Cary-5000) in the 350-3200 nm wavelength range. Electrical resistivity and thermo-emf measurements were done using DC two point probe press contact method in temperature range 300-500 K. Silver paste was employed to ensure good ohmic contacts.

3. Results and discussion

3.1 Growth Kinetics and physical observations

The $Cd_{1-x}Pb_xS$ thin films have been grown onto glass substrates by using chemical bath deposition technique. The triethanolamine is used as a complexing agent to control the precipitation and liquid ammonia is used for better adherence. We tried the deposition of pure CdS thin films at various temperatures from 40 to 90 °C. At 80 °C, a good quality film was obtained. Above and below 80 °C the layer thickness was found to be less as shown in Fig. 1. This can be explained on the basis that, at low temperature most of the ions are not free for the reaction to take place. At increasingly higher temperatures the rate of release of Cd^{2+} and S^{2-} ions are higher, that

enhances the rate of film growth and increases the film thickness up to 80° C. Above this temperature, more and more ions will come out of the bound complex state at a relatively faster rate and therefore the ions may not have sufficient time to condense on the substrate surface, consequently they settle down at the bottom, thus decreasing the layer thickness [3, 26]. Similar procedure was used for the deposition of pure PbS and Cd_{0.5}Pb_{0.5}S and it was observed that the layer thickness for composition x = 1 was maximum as shown in Fig. 1. The time dependence of film growth is shown in Fig.2. It is found that, initially the layer thickness for pure CdS, PbS and $Cd_{0.5}Pb_{0.5}S$ increases with the deposition time and later on it saturates. This may be explained as for smaller deposition time up to 60 min. more and more ions will get deposited on the substrate showing the layer thickness to increase almost linearly. For higher deposition time (>60 min.) the process of depletion of number of ions in the solution causes growth rate to decrease, resulting into saturation of the layer thickness [3, 25-26]. The other parameters namely pH of reaction mixture and speed of substrate rotation was optimized and found to be 10.5 ± 0.1 and 60 rpm respectively. Then the $Cd_{1-x}Pb_xS$ (x = 0 to 1) thin film sample series was deposited onto the well processed glass substrates at the optimized deposition conditions. The deposition process is based on slow release of Cd^{2+} , Pb^{2+} and \hat{S}^{2-} ions.



Fig.1. Variation of film thickness with deposition temperature for chemically deposited $Cd_{1-x}Pb_xS$ (x = 0.0, 0.5, 1.0) thin films.



Fig.2. Variation of film thickness with deposition time for chemically deposited $Cd_{1-x}Pb_xS$ (x = 0.0, 0.5, 1.0) thin films.

The detailed kinetics of film formation can be understood from the following series of reactions. Formation of ammonia ion [27]

(i)

(ii)

(vii)

$$NH_3 + H_2O ----> NH_4^+ + OH^-$$
 (1)

(iii) The reaction of cadmium salt and lead salt with the complexing agent (TEA) to form respective metal complexes [28]

$$Cd^{2+} + n(TEA) \longrightarrow [Cd (TEA)_n]^{2+}$$
 (2)

$$Pb^{2+} + n(TEA) ----> [Pb(TEA)_n]^{2+}$$
 (3)

In the basic aqueous medium these complexing anions decomposes and we get Cd^{2+} (iv) and Pb^{2+} ions

$$[Cd (TEA)_n]^{2+} ----> Cd^{2+} + n(TEA)$$
 (4)

$$[Pb (TEA)_n]^{2+} ----> Pb^{2+} + n(TEA)$$
(5)

(v) The decomposition of thiourea in an alkaline medium releases the sulphide ions as below [26]

$$SC (NH_2)_2 + OH^- ----> CH_2N_2 + H_2O + HS^- HS^- + OH^- ----> S^{2-} + H_2O$$
(6)

The final reaction will be (vi)

(1-x)
$$[Cd (TEA)_n]^{2+} + x [Pb (TEA)_n]^{2+} + S^{2-} + NH_3 -----> Cd_{1-x}Pb_xS + Waste product.$$
 (7)

The color of the deposits changed from orange yellow to black as the composition parameter 'x' was varied from 0 to 1. The terminal thickness of the as-deposited layers went on increasing as shown in Fig.3. Similar thickness trend was observed by G. B. Reddy et al. [29].



Fig.3. Variation of film thickness with composition parameter 'x' for chemically deposited $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films.

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3.2 Structural studies

The XRD patterns of the 'as-grown' Cd_{1-x}Pb_xS films are shown in Fig.4. It is observed that CdS exhibit wurtzite (cubic) and zinc blende (hexagonal) crystal structure. This is in good agreement with earlier report that chemically deposited CdS films depending upon preparative conditions, shows cubic, hexagonal or mixed (cubic + hexagonal) crystal structures [30-31]. The diffractograms indicates that all the samples are polycrystalline in nature over entire range of composition parameter. 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 [32-34]. The shifting of peak position with increase in composition parameter x has not been observed, which indicates that the $Cd_{1,x}Pb_xS$ films are of composite type. Further, analysis showed the presence of oxide phases of cubic CdO, tetragonal PbO and PbO₂, and free elemental sulfur. The presence of oxide phases can be attributed that at pH value larger than 10, excess Cd and Pb can be regarded as being Cd(OH)₂ or CdO and lead oxide due to side reaction, while excess S exist in the form of elemental S arising from the extraneous decomposition of S ions at higher concentrations [35].



2. CdS (200)C
 3. CdS (220) / (110)H
 4. CdS (311) C
 5 S (021) O
 6. PbO₂ (210) T
 7. S (132) O
 8. PbO (111) T
 9.CdS (102) H
 10.S (200) O
 11. PbS (420) C

Fig.4. X-ray diffractograms of chemically deposited $Cd_{l-x}Pb_xS$ ($0 \le x \le 1$) *thin films.*

The lattice parameters 'a' and 'c' for hexagonal phase are calculated by using the relation [36]

$$1/d^{2} = 4/3 \left[(h^{2} + hk + k^{2}) / a^{2} \right] + l^{2} / c^{2}$$
(8)

where h, k, l are the Miller indices and d is the interplanar spacing determined using Bragg's equation. The lattice constant 'a' for cubic phase is obtained using the following relationship [37]

$$a = d \left(h^2 + k^2 + l^2 \right)^{1/2}$$
(9)

The average lattice constants a and c for hexagonal phase are found to have a non-linear variation with composition parameter 'x' in the range from 4.1035 to 4.1720 Å and 6.6061 to 6.7288 Å respectively. The similar trend was observed in case of cubic phase in the range 5.8015 to 5.9171 Å.

The average grain size 'D' of the film samples was calculated by Scherer's formula [38]

$$D = 0.94 \lambda / \beta \cos\theta \tag{10}$$

Where λ is the wavelength of the X-ray used, β is the full width at half maximum and θ is the Bragg angle and tabulated in table 1. It is observed that grain size increases with increase in composition parameter x up to 0.175 and thereafter it decreases with increase in composition parameter.

3.3 SEM and EDAX studies

The seven micrographs of the chemically deposited $Cd_{1-x}Pb_xS$ thin films (20,000 X magnifications) are shown in Fig.5. From these micrographs it is observed that films are of inhomogeneous surface morphology. From these micrographs the average grain size was calculated by intercept method using equation [30],

Average grain size =
$$1.5 \, \text{l/m x n}$$
 (11)

where m is the magnification of the micrograph, 1 is the length of line drawn on the micrograph, n is the number of grains crossed by the line and 1.5 is the parameter assuming spherical grains. The average grain size follows same trend as XRD observation. But, these grain sizes are little bit more than that in XRD observations. This may be due to two or more grains fusing together to form the cluster type of structure.

Fig.6. shows the EDAX pattern of the representative PbS film sample. The pattern confirms the presence of lead and sulpher, in proportion Pb = 60.95 % and S = 39.05 %. The table 2 represents the compositional analysis of seven representative samples, which shows, films are cadmium rich. This may be due to high reactivity of cadmium than sulpher.

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(a) x = 0.00



(b) x = 0.05



(d) x = 0.175



(e) x = 0.20



(f) x = 0.30



(g) x = 1.00

Fig.5(a-g). SEM micrographs of chemically deposited $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films.



Fig 6. EDAX pattern of chemically deposited PbS thin film.

3.4 Optical studies

The optical absorption of the $Cd_{1-x}Pb_xS$ thin films was studied in the wavelength range 350-3200 nm. The variation of optical coefficient with wavelength was further analyzed to find out the nature of the electronic transition across the optical band gap. The nature of the transition was determined using the relation [39],

$$(\alpha h v) = A (h v - E_g)^n //--$$
 (12)

where 'A' is a constant and 'hv' is the energy of photon and n=1/2 for allowed direct transition. The value of absorption coefficient is found to be of the order of 10^4 cm⁻¹ for all composition that supports the direct band gap nature of the semiconductor. Fig.7. shows the plot of $(\alpha hv)^2$ versus hv whose intercept on energy axis at $\alpha = 0$ gives the band gap energy E_g of films and are cited in table 1. It is observed that band gap decreased with increase in composition parameter 'x'. The reason for this may be attributed to the increase in thickness [40].



Fig. 7. Plot of $(ahv)^2$ versus hv for chemically deposited $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films.

3.5. Electrical studies

The dark dc electrical resistivity of these films was studied in the temperature range of 300-500 K by using DC two point press contact method. The variation of log resistivity with reciprocal of temperature is shown in Fig.8. It shows that all the films are of semiconducting type. The non-linear nature of the plots attributes the presence of many defect levels in the films. It is observed that the room temperature electrical conductivity increases continuously with increase in 'x' up to 0.175 and further it decreases up to x = 1 as shown in Fig. 9. This increase in electrical conductivity of CdS and PbS are 6.13×10^{-7} and 1.70×10^{-6} (Ω cm)⁻¹ respectively. These values of electrical conductivity agree well with the reported values [41-42]. The highest conductivity is found to be 7.94×10^{-6} (Ω cm)⁻¹ for the composition x = 0.175. The lower magnitudes of electrical conductivity of the films are attributed to the deposition method itself i.e. generally, chemical methods result into lower magnitudes of electrical conductivity [30].



Fig.8. Variation of log ρ with reciprocal of temperature for chemically deposited $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films.



Fig.9. Variation of electrical conductivity with composition parmeter 'x' for chemically deposited $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films.

Thermo-emf generated by the samples was measured in the temperature range 300-500 K and the obtained plots are as shown in Fig.10. These variations are found to be non-linear with n-type conduction. The non-linearity indicates non-degeneracy of the material whose thermoelectric power is proportional to n^{th} power of absolute temperature.



Fig.10. Variation of thermo-emf with temperature difference for chemically deposited $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films.

Composition 'x'	Grain size D(nm)	Band gap energy Eg (eV)	
0.000	7.0	2.47	
0.025	9.5	2.41	
0.050	10.0	2.38	
0.075	10.7	2.32	
0.100	11.4	2.28	
0.125	12.2	2.24	
0.150	14.2	2.18	
0.175	17.0	2.13	
0.200	15.5	2.04	
0.300	12.0	1.86	
0.500	10.1	1.47	
0.700	8.8	1.01	
0.800	8.1	0.85	
1.000	7.5	0.49	

Table 1. Some of the characteristic parameters of $Cd_{1-x}Pb_xS$ thin film structures

Table 2. Elemental composition of $Cd_{1-x}Pb_xS$ thin films deposited by chemical bath method.

Film composition

As taken atomic percentage

	In bath solution (%)			in film by EDAX analysis (%)		
	Cd	Pb	S	Cd	Pb	S
CdS	50.00	00.00	50.00	57.45	00.00	42.55
Cd _{0.95} Pb _{0.05} S	47.50	02.50	50.00	54.67	02.42	42.91
Cd _{0.875} Pb _{0.125} S	43.75	06.25	50.00	52.03	05.37	42.60
Cd _{0.825} Pb _{0.175} S	41.25	08.75	50.00	53.87	08.25	37.88
$Cd_{0.5}Pb_{0.5}S$	25.00	25.00	50.00	29.68	26.56	43.76
PbS	00.00	50.00	50.00	00.00	60.95	39.05

4. Conclusions

In conclusion, $Cd_{1-x}Pb_xS$ ($0 \le x \le 1$) thin films can be deposited by simple chemical bath deposition technique. XRD studies revealed that these films are polycrystalline in nature, exhibiting the mixed cubic and hexagonal structure for CdS and only cubic structure for PbS. Films with crystallite size in the range 7-17 nm can be obtained. EDAX studies showed that films are non-stoichiometric. The optical band gap engineering could be realized in the $Cd_{1-x}Pb_xS$ thin films with help of modulating the composition parameter 'x'. All the films are of semiconducting nature with n-type conductivity. The relatively better electrical and structural properties are shown by film with x = 0.175 which is useful in both photoelectrochemical and solar cell applications.

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