



ROLE OF Pb^{2+} IONS AS THE GROWTH AND STRUCTURE DIRECTING AGENT IN (Cd- Pb)S SOLID SOLUTIONS

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ABSTRACT

This paper reports some interesting observations related to effect of Pb^{2+} ion concentration variation on the crystal growth habits and morphology of (Cd-Pb)S solid solutions. (Cd-Pb)S films were prepared by CBD technique. XRD studies show a cubic structure consisting of independent XRD planes for both CdS and PbS. The transformation from polycrystalline to a single crystalline phase with increasing Pb^{2+} ion concentrations was evident in the XRD patterns. The crystal size was diminished remarkably with increasing Pb^{2+} concentration. The SEM studies show growth of leaf like fractal patterns in (Cd-Pb)S films. A denser growth was observed at higher Pb^{2+} concentration. Results of PC rise and decay are presented for different (Cd-Pb)S films. A high gain was observed in (Cd-Pb)S samples with a minimum concentration (2%) of Pb. The PC decay studies were employed for the calculation of some important electronic parameters like conductivity, mobility and trap depth for the prepared films.

Keywords: Photoconductivity (PC); Solid Solutions; Chemical Bath Deposition (CBD); II-VI Compounds; Crystal Growth.

I. INTRODUCTION

II-VI group compound semiconductors are important materials for harvesting energy from sunlight through photovoltaic devices. Various methods of preparations have been introduced to prepare nano- or micro scaled II-VI particles in various sizes and morphologies over the past few years of preparations like electrode position (ED), spray pyrolysis (SP), chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), molecular beam epitaxy (MBE), and physical vapour deposition (PVD) [1-6]. Among all these, a simple solution synthesis is the most cost effective way to prepare these materials at relatively low temperatures with a considerable control over the size and morphology of the as-prepared samples. Nano materials show size and morphology dependent electrical and optical properties. Therefore, development of methods of synthesis of nanoparticles with controlled morphology is important for exploring their potential further. In the present work (Cd - Pb) S was selected as base material. CdS have a direct band gap nature while PbS has both direct and indirect band gaps. We have recently devoted time to synthesize (Cd-Pb)S in order to study their structure and morphology-dependent optical properties. There have been a number of studies on mixed base (Cd-Pb)S films

prepared by CBD . As reported by Nair et al [7-9] and Bhushan, et al [10-12], the films deposited by CBD method [13-15] are quite important for PC studies. While the former group found improvement in the optoelectronic characteristics of solar assisted chemically deposited films, the latter group reported improvement in (Cd - Pb)S (mixed base) films. CdS thin films were grown by the CBD method by O.V. Galan et al. also [16]. So in present case CBD method was used for depositing (Cd-Pb)S films with different concentrations of Pb^{2+} ions like 2%, 5% ,10% and 50% .

It is known that CdS and PbS have different crystal parameters and there is a vast difference in their band gaps. So it would be interesting to observe the crystal growth habit when these two widely different materials are mixed in various proportions. This study investigates a simple and cost effective method for structure and morphology controlled growth of these technologically important nanomaterials. The solubility of CdS and PbS at room temperature and normal pressure is very low. The application of crystal growth inhibitors is a common technique used for the precipitation and dissolution of sparingly soluble salts from aqueous solution in a wide range of technologically important processes such as mineral processing, petroleum recovery, geothermal, pulp and paper industry, production of potable water, and industrial water treatment [17]. The commonly used inhibitors include polymers or metal ions .The role of inhibitor is not only to prevent the precipitation of sparingly soluble salts from aqueous solutions but also to enhance the solubility of the foreign materials used as dopant. Therefore, a fundamental knowledge of the solution properties of inhibitors is of vital importance in developing high performance formulations for achieving optimum system efficiency. Fleish, Bisaz&Russel [18] have demonstrated that Pb^{2+} promotes the precipitation under physiological conditions i.e lower ionic strength and temperature, so this study will be useful for applications of Pb^{2+} ions as a crystal growth inhibitor.

The object of the present investigation is a systematic screening of Pb^{2+} metal ions for their effects on the reaction crystallization of (Cd- Pb)S solid solutions and the transformation of (Cd-Pb)S solid solutions from polycrystalline to a single crystalline phase. In the crystallization process of (Cd-Pb)S the concentration of Pb^{2+} was varied from 2%,to 50% of the Cd $^{2+}$ concentration; we regard this level as the upper limit for a study of inhibition in the proper sense. In the hydrolysis experiments different levels of foreign metal ion concentration were chosen to find the range of transition from weak to strong inhibition. In this paper, we describe the role of structure and morphology of as obtained (Cd-Pb)S nano materials on their PC properties. Study of PC is important on one hand, due to its wide technological applications such as electro-photography, image intensifiers, light meters, thin film electronics, solar cells and television cameras, etc.[19] and on the other hand, due to a number of physical processes involved; which provides various aspects of study.The Phenomenon of photoconductivity can be obtained in pure form of the materials known as intrinsic photoconductivity or in presence of impurities or crystal imperfections known as impurity or imperfection photoconductivity. The room-temperature photoconductivity of the as-prepared (Cd–Pb)S films significantly depends on their crystallinity and morphology. The percentage of PbS was varied up to 50% and a sufficiently high value of I_{pc}/I_{dc} was observed under visible excitation. The values of lifetime, mobility and trap depths have been calculated from the PC decay curves. A discussion has been presented on the nature of PC rise and decay curves.

II. MATERIALS AND METHODS

The films were prepared on 24x75 mm commercial microscopic glass slides by the CBD method at a constant temperature of 60° C and pH around 11.2. The glass substrates were washed with acetone and distilled water, dried in hot air and finally dipped in a beaker containing a mixture of acetates of lead and cadmium, thio-urea, tri-ethanolamine (TEA) and 30% aqueous ammonia for 1 hour. Films were deposited under static conditions. After deposition, the slides were washed with a jet of double distilled water, dried in air and annealed at 350°C for 1hr under ambient atmosphere. SEM studies were performed using LEO (430) SEM. XRD was studied by using a computerized Philips diffractometer with CuK_α radiation. PC rise and decay was measured with an indigenously did set up.

III. RESULTS AND DISCUSSIONS

3.1 Crystal Growth Mechanism and Evolution of Fractal Morphology

(Cd –Pb)S films obtained in the present study indicates decreased fractal dimension and increased density with the increasing concentration of Pb^{2+} ions as can be observed in Fig 1(a - e). Growth of cabbage like fractal structures is observed with increasing percentage of PbS. Indicate formation of a 2D leafy structure of the material in the initial state. These planes can be grown on the structural defects like stacking fault or grain boundaries created due to the lattice mismatch and strain. Under continued growth condition these 2D structures formed cabbage like 3D structures. The growth of 3D structure enhanced with the increasing Pb %. So the presence of PbS helped in a 3D crystal growth.

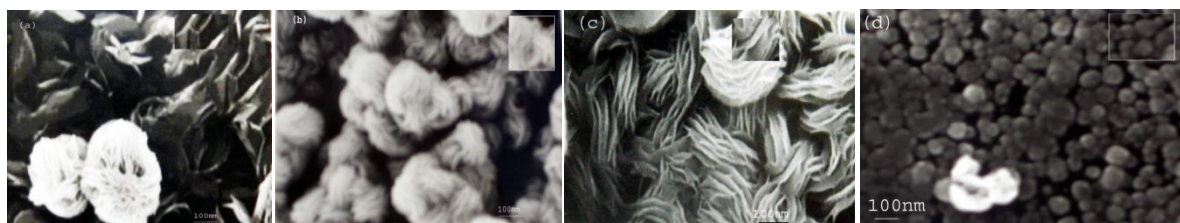


Fig 1 : SEM micrograph different composition of (Cd-Pb) S film at magnification X 10K on glass substrates in static condition (a) CdS (b) $(\text{Cd}_{0.95}\text{-Pb}_{0.05})\text{S}$ (c) $(\text{Cd}_{0.90}\text{-Pb}_{0.10})\text{S}$ (d) $(\text{Cd}_{0.50}\text{-Pb}_{0.50})\text{S}$

In solution based synthesis, the crystal formation process can be divided into two stages of nucleation and crystal growth. External conditions dominate the nucleation and growth process and affect the size and morphology of a crystal. The growth mechanism of NPs can be explained by initiating changes in the reaction parameters. CBD is a low temperature method in which rearrangements and diffusion of NPs has been limited to the initial stage, favouring the diffusion limited aggregation (DLA) theory [20-22], where reactant concentration remains invariant. In the initial reaction period, aggregation affects the overall size instead of the morphology. But, as the reaction time extends further, the diffusion process becomes dominant with decreasing reactant concentration. In the DLA model, the morphology control can be achieved through the parameters like sticking coefficient [23], which depends on solvents, which helps in achieving the fractal patterns as flower, prickly sphere, and snowflake etc. In present case aqueous solutions were used as precursors, the reactants disperse more homogeneously in H_2O and are grown under less confinement in a boiling droplet of solvent, which finally leads to a flowerlike morphology of (Cd –Pb)S in H_2O . According to the proposed mechanism the formation of

an individual pattern such as prism- and rodlike (Cd –Pb) S was easier than dendritic or fractal patterns such as flowerlike or snow flake like(Cd –Pb) S, if a solvent with a high saturated vapor pressure such as ethanol was utilized as reaction media. The polarity and saturated vapor pressure of the solvents affects the homogenization of the reactants in the reaction medium, the amount of individual nucleus formation, and the amalgamation and direction preference of growing nucleus under thermal condition.

Further, the basicity is important in controlling the morphologies of typical flowerlike (Cd–Pb) S. Various solution basicities give rise to different crystal growth rate along certain crystal faces. Such as crystal growth habit leads to the flowerlike shape. In the present case a weak base NH₄OH was used, where NH₃, as one of the by-products, can prevent the merger of the nucleus in the supersaturated solvents, supporting the formation of a regular polyhedral shape. Since all the precursors have been prepared in H₂O which naturally produce Cd (OH)₄²⁻ / Pb (OH)₄²⁻ after hydrolysis, they favor the fractal growth despite using a weak base like NH₃. Cd (OH)₄²⁻/ Pb (OH)₄²⁻ precursors play an important role in determining the morphologies of the crystal due to the concentration of OH⁻ in the reaction solution, which lead to the formation of an anisotropic particle such as flowers, snowflakes, and prickly sphere like morphology. Further, TEA was used as a complexing agent in the present study, which slowed down the release of CD / Pb ions into the solution, which in turn helped in controlling the particle size and morphology of the NPs.

The mechanism of deposition of (Cd-Pb)S films is similar to that of CdS. Deposition of CdS is based on the slow release of Cd⁺⁺ and S⁻ ions in an aqueous alkaline bath and subsequent condensation of these ions on the substrates suitably mounted in the bath. The slow release of Cd⁺⁺ ions is achieved by dissociation of a complex species of cadmium Cd (TEA)⁺⁺. The availability of Cd⁺⁺ ions is governed by the following dissociation equilibrium



The S⁻ ions are provided by the dissociation of thiourea [SC (NH₂)₂] in the ammoniac medium as follows



Since the solubility of CdS is low ,even very low concentrations of Cd⁺⁺, Pb⁺⁺ and S⁻ ions released, according to equations (1, 2 &3) are sufficient to yield the solid phase.

3.2 Role of Pb²⁺ ion on Crystal Growth and Morphology

CdS and Pubs have different crystal structures. In the present study a decrease in particle size with an increase in the Pb ion concentration was observed. During co-precipitation of amorphous CdS and PbS regular crystals are obtained when the nucleation rate is reduced due to super-saturation with respect to a particular structure. The increased proportion of regular crystals in the presence of Pb²⁺ lowers the super saturation by initial precipitation of another phase. Reduction of average crystal size in comparison with the bulk may be caused by promotion of nucleation, inhibition of crystal growth, or both. Inhibition of crystal growth is caused by adsorption of the inhibitor, and so is most probably inhibition of nucleation. The inhibitor being adsorbed to minute nuclei prevents their further development. It has been reported that an increase in Pb²⁺ concentration causes highly significant decrease in crystal dimensions without any noticeable morphological effect. However, growth inhibition is usually accompanied by irregular growth, because adsorption is not uniform, or growth rate

fluctuates in space and time. If the degree of adsorption is different for different crystal faces, then habit modification results. In the present case a change in crystal habit was quite evident in the XRD pattern of (Cd-Pb)S Fig. 2(a - e), discussed in detail later.

Inhibition of heterogeneous nucleation of crystals may take place either by inhibiting growth of the nuclei or by poisoning the substrate, thereby hindering the initial stage of the process. The time taken by the nucleus to grow to a critical size increase in the presence of a growth inhibitor [24]. The latter mechanism has been used to explain inhibition by Pb^{2+} , which gradually disappears from solution by adsorption and subsequent solid-state diffusion into the CdS crystals [25]. The emergence of single PbS peak in the XRD pattern in Fig.2(d) for higher Pb concentration further supports the second mechanism.

3.3 XRD Studies

The XRD studies were performed to study crystal structure and to determine lattice constants fig.2(a-e) shows the X-ray diffractogram of (Cd-Pb)S films.

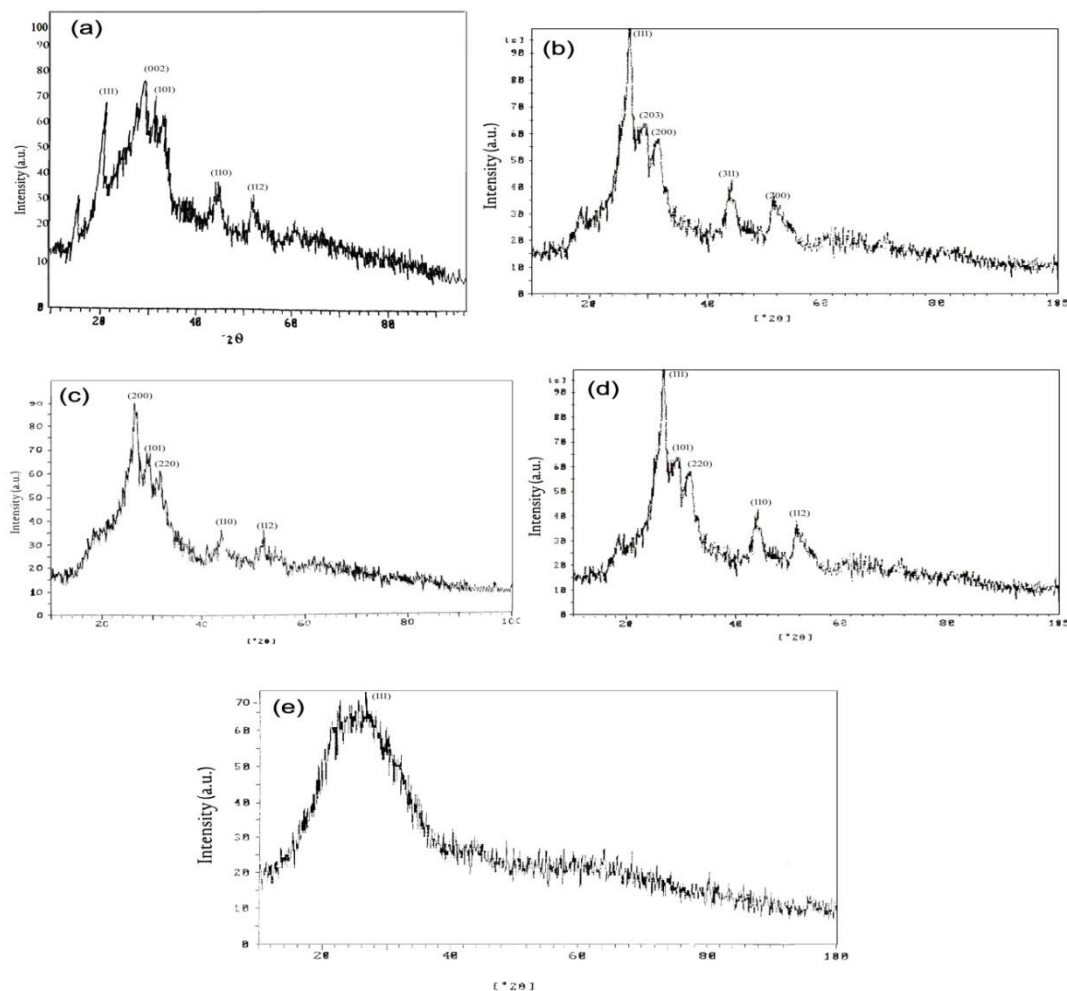


Fig 2: X Ray diffractograph of (a) CdS (b) $(Cd_{0.98}Pb_{0.02})S$ (c) $(Cd_{0.95}-Pb_{0.05})S$ (d) $(Cd_{0.90}-Pb_{0.10})S$ (e) $(Cd_{0.50}-Pb_{0.50})S$ thin films.

Different peaks are assigned by comparing with the standard ASTM data. It is observed from the results of the XRD that by increasing the percentage of PbS, the polycrystalline nature of CdS disappeared and a single phase

with smaller particle size were obtained This shows a growth inhibition process with increasing percentage of Pb [26]. Similar observations are reported earlier also for the solution based synthesis of (Cd – Pb) S solid solutions, where it was observed that the lattice parameters of the various mixtures did not vary appreciably , but a single phase of CdS is observed in the best cases. In the nanocrystalline CdS, both rock salt (at high pressure) and Zinc blend (at ambient) structures are observed. A transition from wurtzite to rock-salt transformation involves not only a change in symmetry (hexagonal to cubic) but also a change in coordination number (from four to six). The two types of transitions are affected by the particle size. The equilibrium crystal structure tends to change from wurtzite to the cubic as the particle size of CdS decreases [27]. In the present study it was observed that with increasing percentage of PbS the crystal size decreased and a single cubic phase of PbS emerged. So it may be concluded that a size induced structure transformation takes place with increasing percentage of PbS.

3.3.1 Structural transformation and strain calculations:

The lattice parameters have been measured by XRD as a function of % Pb content in (Cd-Pb)S thin films. The lattice parameters were calculated for (200), (111) and (311) peaks and the results were quite similar. The solid lines shown in Fig. 3 shows a linear variation in lattice parameters as a function of composition of different (Cd-Pb) S solid solutions.This shows that (Cd-Pb)S solutions obeys the Vegard’s law.Vegard’s law can be represented by the following relation;

$$a(\text{Cd-Pb})\text{S} = x a_{(\text{Cd})} + (1-x)a_{\text{Pb}} \dots \dots \dots (4)$$

Further, a linear relation between the composition of solid solution of (Cd - Pb) S and their lattice constants was obtained which confirms the Vegard’s law as can be observed in Fig. 3

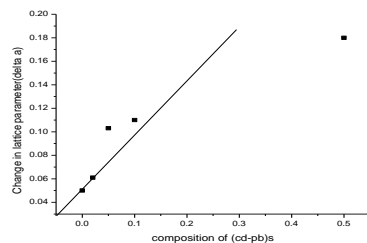


Fig 3: Vegard’s law showing a linear variation of composition of (Cd-Pb)S Vs change in lattice parameter

The difference between the standard and the experimental value of lattice parameters calculated on the basis of the peak positions suggest the presence of strain in the crystal, which might explain the deviation in the crystal lattice. Strain also affects the peak width. Relatively large values of strain together with an increase in lattice parameters were found for PbS precipitated by thiourea[28]. The expanded lattice was due to either a non-equilibrium state or more specifically, vacancies in the crystal. Besides providing a measure of different composition of films XRD also shows a correlation between the amount of Pb in the film and FWHM of the peaks. The FWHM increases almost linearly with increase in Pb content up to the maximum single phase solution. Further, Williamson-Hall (WH) analysis is a simplified integral breadth method for estimating particle size and strain in the lattice which was employed in the present study to correlate the strain and particle sizes [29-30]. The inter-planer distances (dhkl) for each diffraction angle have been calculated using Bragg’s law

$$d_{hkl} = n \cdot \lambda / 2 \sin \theta \dots \dots \dots (5)$$

Where λ is X ray wavelength ($\lambda=1.54059292\text{\AA}$) and θ is Bragg's diffraction angle.

The crystallite's size of crystals has been calculated by using Scherrer's formula.

$$D=0.9\lambda/ \beta.\cos\theta \quad \dots\dots\dots (6)$$

The crystallite size and strain have been further determined using a Modified form of Williamson Hall (MWH) relation, from the plot of $\beta/\tan\theta = f(1/\sin\theta)$ using the equation below[29]:

$$B/\tan\theta = (k. \lambda/D).1/\sin\theta +4\varepsilon \quad \dots\dots\dots (7)$$

Where ε is strain and k is the constant. The crystallite size can be calculated from the slope ($k. \lambda/D$) and the strain ($4.\varepsilon$) from the intercept of the plot $\beta/\tan\theta = f(1/\sin\theta)$. The crystallite size and strain can be calculated from the slope and from the intercept respectively, of the MWH plots for different (Cd-Pb) S samples.

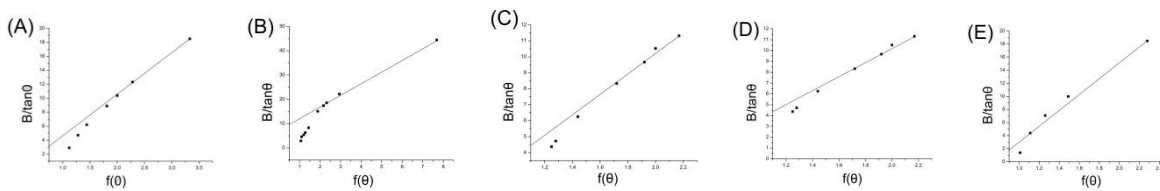


Fig.4: Williamson-Hall (W-H) plots of $1/\sin\theta$ Vs $\beta/\tan\theta$ for different composition of (Cd-Pb)S - (A) CdS (B) $(\text{Cd}_{0.98}\text{-Pb}_{0.02})\text{S}$ (C) $(\text{Cd}_{0.95}\text{-Pb}_{0.05})\text{S}$ (D) $\text{Cd}_{0.90}\text{-Pb}_{0.10})\text{S}$ (E) $(\text{Cd}_{0.50}\text{-Pb}_{0.50})\text{S}$.

The particle sizes calculated through strain studies matches with those calculated by Scherrer's formula as compiled in table- I

Table- I Values of particle size, dislocation densities & strain for different (Cd-Pb)S films.

S.No	Systems	Particle size(nm)from		Dislocation dens (δ)	Strain ε
		XRD	W.H. Plots		
1.	Cds	10.8	11.4	0.08×10^{-4}	0.625
2.	$(\text{Cd}_{0.98}\text{-Pb}_{0.02})\text{S}$	5.2	5.1	1.8×10^{-4}	0.75
3.	$(\text{Cd}_{0.95}\text{-Pb}_{0.05})\text{S}$	3.3	3.4	2.4×10^{-4}	1
4.	$(\text{Cd}_{0.90}\text{-Pb}_{0.10})\text{S}$	2.1	2.5	3.4×10^{-4}	1.1
5.	$(\text{Cd}_{0.50}\text{-Pb}_{0.50})\text{S}$	1.07	1.04	9.8×10^{-4}	3

3.4 PC Rise and Decay Studies

In present work PC rise and decay in (Cd-Pb) S films were also studied. The graphs for CdS, $(\text{Cd}_{0.98}\text{-Pb}_{0.02})\text{S}$, $(\text{Cd}_{0.95}\text{-Pb}_{0.05})\text{S}$ and $(\text{Cd}_{0.90}\text{-Pb}_{0.10})\text{S}$, $(\text{Cd}_{0.50}\text{-Pb}_{0.50})\text{S}$. films are shown in Fig 5. The general nature of the graph is similar for all the films. This is characterized by a fast rise in the beginning followed by saturation. The latter sets in when the recombination becomes predominant. Due to absorption of light, electron-hole pairs are created which give rise to photoconductivity due to movement in their respective bands. The hole then diffuses to impurity centre where it captures the electron from the centre and gives rise to emission. Finally electron wandering in the conduction band is captured by the centre with a release of small amount of energy as infrared radiation of vibrational quanta. Since the luminescent transitions and the capture of free electrons occur in different parts of the cycle, a difference in time constants of decay of photoconductivity is expected.

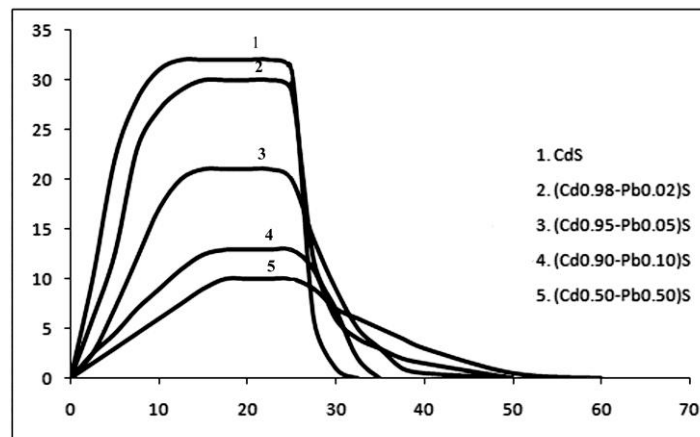


Fig 5: Rise and Decay Curve of Different Composition of (Cd-Pb) S film

Table II summarizes the dark current I_{dc} and the ratio I_{pc}/I_{dc} for a number of films.

TABLE- II Values of dark current (I_{dc}), photo current(I_{pc})and the ratio (I_{pc}/I_{dc}) for differentfilms(Temp. of deposition= $60^{\circ}C$, time of deposition =1 hr., voltage =15volts.)

S.N.	System	I_{dc}	I_{pc}	I_{dc}/I_{pc}
1	CdS	0.1	32	3.2×10^6
2	(Cd0.98-Pb.02)S	0.05	30	6×10^6
3	(Cd0.95-Pb.05)S	0.1	21	2.1×10^6
4	(Cd0.90-Pb.10)S	0.1	13	1.3×10^6
5	(Cd0.50-Pb.50)S	0.1	10	1.05×10^6

Decay curves can be expressed by the expression,

$$i = i_0 / (1 + at)^b \tag{8}$$

Where ‘a’ and ‘b’ are constants which may vary with light intensity and temperature during the decay time. The growth and decay curves must include the contributions of the traps. The probability of an electron (hole) escaping from a trap with depth E and cross-section for the capture of an electron (hole) S_t , at a temperature T, is given by

$$P = N_{eff} \cdot V S_t \exp (-E/kit) \tag{9}$$

Where N_{eff} is the effective density of states in conduction (valance) band. If the probability of replacing of freed electrons by empty traps is neglected, the rate of change of trapped electrons during decay is

$$dn_t/dt = -n_t P \tag{10}$$

The solution of the above equation is

$$n_t = n_{t0} e^{-Pt} \tag{11}$$

The lifetime $\tau = \{v S_r N_r\}^{-1}$ can usually be considered a constant, especially if $n \ll N_r$, the density of holes in recombination centers. Then the decay can be written as

$$n_t = n_{t0} \tau P e^{-Pt} \tag{12}$$

A major effect of trapping is to make the experimentally observed decay time of photocurrent longer than the carrier lifetime. In the absence of trapping, the observed photocurrent will decay in the same way as the density of free carriers and thus, the observed decay time will be equal to the carrier lifetime. Decay curves also depend upon temperature and light intensity. The shape of such curves is modified due to trap filling and emptying. If one type of trap is involved the decay is of exponential type and if trap of different depths are involved the resulting decay can be observed as a combination of many exponentials. From the exponential decay the trap depths can be easily determined. From the decay curves the values of lifetime, mobility and trap depths have been calculated and the results are compiled in table III.

TABLE-III Values of instantaneous lifetime (τ), mobility (μ) and trap depths (E_1 and E_2) for different (Cd-Pb)S films. (Temp. of deposition =60⁰C, time of deposition =1 hr., voltage =15volts.)

S.N	System	Lifetime τ (sec)	Mobility μ (cm ² /v-sec)	Trap depth
1	CdS	19.89	42.90	E1=0.771,E2=0.712
2	(Cd0.98-Pb.02)S	34.30	53.3	E1=0.502,E2=0.538
3	(Cd0.95-Pb.05)S	31.11	51.4	E1=0.505,E2=0.567
4	(Cd0.90-Pb.10)S	24.4	22.4	E1=0.792,E2=0.773
5	(Cd0.50-Pb.50)S	21.6	12.4	E1=0.797,E2=0.778

3.5 Effect of Particle Size, Defects and Dislocations on Photocurrent

The photocurrent depends on a lot of parameters like a life time, mobility, diffusion of free carriers, etc. These properties intrinsically depend on the crystal morphology, structure and defects present .Dislocations, grain boundaries and stacking faults are some common defects present in solution processed crystals. The maximum photocurrent was observed in (Cd-Pb) S solid solutions when the least amount of PbS is included (2%). Earlier workers considered the component of the photocurrent in (Cd-Pb) S films is due to enhanced mobility [30]. As the amount of PbS increased the photocurrent decreased substantially. This can be related to the fact that the particle size decreased with increase in PbS%. This in turn increases the surface to volume ratio. The defects present at the grain boundaries of individual crystals also increases with the diminishing size of crystals. The particle size, dislocation densities& strain for various composition of (Cd-Pb)S is compiled in table V. Dislocation densities also increases with decreasing particle size. It is known that grain boundaries and dislocations offer relatively little resistance to diffusion of atoms in comparison with diffusion to perfect crystals. A dislocation is an open passage for diffusion. Diffusion is greater in plastically deformed material and it decreases when the crystals are annealed. In present case also the photocurrent increase substantially when the films were annealed at 400⁰c in ambient atmosphere.Earlier

workers have attributed the increase in photocurrent in (Cd – Pb)S to enhance mobility. In present study too we observe maximum mobility for 2% PbS.

IV. CONCLUSIONS

(Cd – Pb)S mixed base films were prepared by a simple and cost effective method. The mechanism of size and morphology control of (Cd – Pb)S solid solution by Pb^{2+} ions on the nucleation and growth process is described. The XRD studies show emergence of a single crystalline phase with increasing percentage of PbS. The mechanism of nucleation, crystal growth and inhibition is discussed in detail to explain the changes observed in the crystal growth habit with increasing percentage of PbS. The PC studies show maximum PC gain with a minimum % of Pb incorporation. The nature of rise and decay curves is explained and this study was used to calculate some important electronic parameters of (Cd-Pb)s solid solutions.

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