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Photoconducting and photovoltaic studies on some chemically deposited (Cd-Zn)S & (Cd-Pb)S films

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Results of photoconductivity (PC) rise-decay and excitation spectra, optical absorption spectra and photovoltaic (PV) studies are presented for some (Cd-Zn)S & (Cd-Pb)S films, prepared in presence of $CdCl_2$ as flux and La & Pr as impurities. The nature of rise and decay curves are discussed and values of lifetime, mobility and trap depth are presented. Lifetime & mobility improve in presence of impurities, which may be responsible factors for high sensitization in photoconductivity. Band gaps of the materials are evaluated from PC excitation spectra and optical absorption spectra. Values of short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor and efficiency corresponding to PV studies are also presented. Efficiencies of the order of 3.12–3.71% are found.

1. Introduction

Thin film studies of CdS type materials are important because of their wide application as sensitive photoconductor, I-R detectors and solar cells etc. It is always useful to prepare highly sensitive PC films by economically cheaper methods. Earlier workers used sophisticated techniques like vacuum evaporation, spray pyrolysis, sputtering and molecular beam epitaxy methods [1] for the preparation of films of such materials. Bhushan and co-workers used chemical deposition technique and reported quite high photo to dark current ratios in such films [2–6]. Alongwith PC studies utility of chemical deposition method in the deposition of metal chalcoginde thin films were reviewed by Mane and Lokhande [7]. Bhushan and co-workers also reported photoluminescence under UV (3650Å) excitation and electro-luminescence under A.C. field excitation in such films. The PV measurements of these films appeared to be important in view of high photoconduction observed by these workers. The present paper thus, reports the PV studies of some (Cd-Zn)S and (Cd-Pb)S films under visible excitations. Results of PC are also presented for the films not studied earlier.

2. Experimental details

The films were prepared on substrates of microscopic glass slides/conducting glass plates of dimension (24 mm × 75 mm). Conducting glass plates were used for the films of PV studies. The conducting glass plates were prepared by depositing SnO_2 conducting layer by spray pyrolysis method using $SnCl_2 \cdot 2H_2O$ as the original chemical. The resistivity of the plates thus prepared was $\sim 20\ \Omega/cm^2$. The substrates were cleaned with acetone and distilled water and were dipped vertically into a mixture of 1 M cadmimum acetate (7 ml) and thiourea (7 ml), triethanolamine (2 ml) and 30% aqueous ammonia (25 ml), [all AR grade 99.9% pure]. For preparing films of mixed base [(Cd-Zn)S and (Cd-Pb)S] appropriate amounts of zinc acetate and lead acetate were also mixed in the original mixture. The solutions were prepared in double distilled water and the pH value of mixture was about 11. Doped films were prepared by adding to the original mixture 0.01 M solution of 99.9% pure $CdCl_2$ [volumes varied from 4–12 ml; best results observed for 10 ml] and nitrates of lanthanum and praseodymium [volumes varied from 1–5 ml; best result obtained for 2 ml La and 3 ml Pr] together as well as separately. The depositions were made at a temperature of 60°C in a water bath. The deposition of films is based on precipitation followed by condensatation. In the beginning when precipitation started, stirring was done. After that the deposition was made in the static condition. After depositions films were cleaned with distilled water and then dried by keeping the films in open atmosphere at room temperature. The thickness of the films were measured by mass difference method using a microbalance and were found to lie between 1.997–2.083 μm for different films.

For PC studies co-planar electrodes (1.5 mm wide and 24 mm long at a separation of 2 mm) were formed by applying colloidal silver paint to the surface of the film. The photocurrents were measured by exposing the total area and also by removing the uncovered area beyond the electrodes. It was found that the photocurrent

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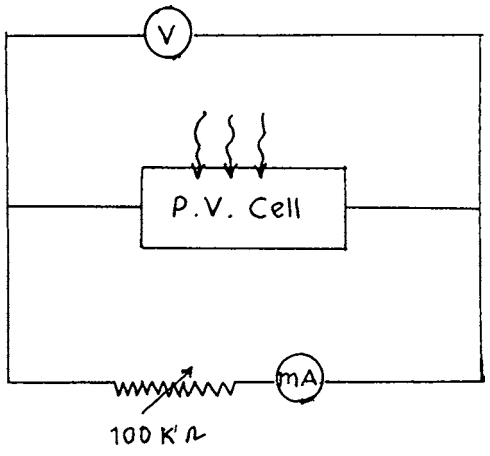

Figure 1 Circuit diagram for photovoltaic studies.

was little higher in the later case. All the results mentioned in this paper are corresponding to the later case. For PV measurements silver electrode in 1 cm^2 area was painted on the back surface of the film. The PC rise and decay studies were made by exciting with incandescent bulbs of 100 W(power 18 mW)and noting the photocurrent as a function of time by a nanometer (DNM-121). For PC excitation spectral studies different wavelengths were selected by passing the radiation from an incandescent bulb of 1 kW through a prism monochromator and noting the photocurrent corresponding to different exciting wavelengths thus obtained. PV studies were made by using a bulb of 100 W(power 2 mW). The current and voltage were measured by using earlier mentioned nanometer and a digital multimeter [scientific HM 5011-3] respectively. A circuit shown in Fig. 1 was used for this purpose.

3. Results and discussions

3.1. PC studies

Figs 2 and 3 show the rise and decay curves of different (Cd-Pb)S and (Cd-Zn)S films respectively using $CdCl_2$ as flux and La and Pr as the impurities. The corresponding data of dark current (I_{dc}), photocurrent(I_{pc})and the ratio of (I_{pc}/I_{dc}) are summarized in Table I. It is observed that with increasing concentration of Pb the I_{dc} increases and I_{pc} decreases and by increasing the Zn concentration, the I_{dc} decreases and I_{pc} increases. Therefore, the highest value of the ratio I_{pc}/I_{dc} is found for the combination 95:5 of Cd to Pb and 80:20 of Cd to Zn. Presence of impurities also affects the values of the ratio I_{pc}/I_{dc}. Nair *et al.* [7, 8] reported dark conductivity $= 2 \times 10^9\ (\Omega cm)^{-1}$ and photosensitivity giving $I_{pc}/I_{dc} = 10^6$ for CdS films prepared in presence of solar radiation. They called this method as solar-assisted chemical deposition technique. In the present case the films were prepared in the laboratory under daylight.

The general nature of rise and decay curves is similar in the different doped cases. In these cases the rise comprise of fast increase in the beginning due to generation of carriers followed by saturation resulting due to balancing effect of generation and recombination phenomena. In the case of undoped systems [CdS and (Cd-Pb)S in Fig. 2 and CdS and (Cd-Zn)S in Fig. 3], the rise is comparatively slower. It seems that more recombination centers occur in the undoped systems which are reduced due to compensation in presence of impurities. Hence the rise becomes faster in later case. Similarly decay of PC shows a fast decrease due to recombination and slow variation arises due to trapping effect. It is further noted that in (Cd-Zn)S due

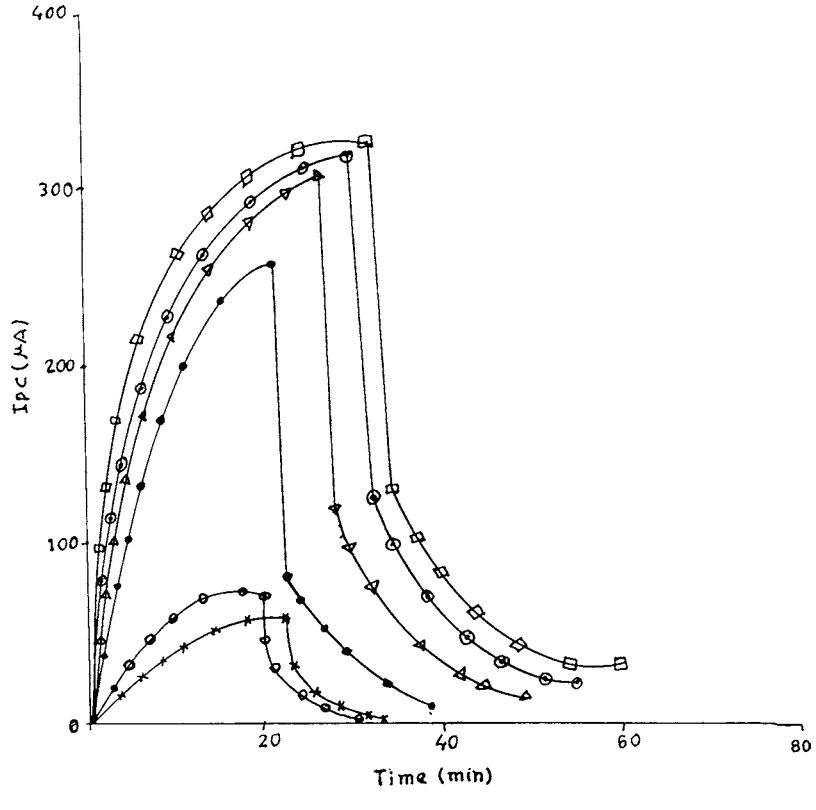

Figure 2 Rise and decay curves of different (Cd-Pb)S films [incident radiation power = 18 mW; film thickness (1.997–2.083) μm]. 1. (x) CdS; 2. (°) (Cd_{95}-$Pb_{.05}$)S; 3. (●) (Cd_{95}-Pb_{05})S:$CdCl_2$; 4. (△) (Cd_{95}-Pb_{05})S:$CdCl_2$La; 5. (⊘) (Cd_{95}-Pb_{05})S:$CdCl_2$, Pr; 6 (□) (Cd_{95}-Pb_{05})S;$CdCl_2$, La, Pr.

TABLE I Values of dark current (I_{dc}), Photocurrent (I_{pc}) and the ratio of (I_{pc}/I_{dc}) for different films under three conditions (temperature of deposition = 60°C, Time deposition = 1 hour, Voltage = 15 volts), annealing temperature = 300°C, annealing time = 5 min

		For the total film unannealed			Annealed			Annealed for the film containing the central part only		
S. no.	System	I_{dc} (nA)	I_{pc} (μA)	I_{pc}/I_{dc}	I_{dc} (nA)	I_{pc} (μA)	I_{pc}/I_{dc}	I_{dc} (nA)	I_{pc}(μA)	I_{pc}/I_{dc}
1	CdS	0.2	58	2.9×10^5	0.1	60	6×10^5	0.1	80	8×10^5
2	$(Cd_{95}\text{-}Pb_{05})S$	0.05	67	1.34×10^6	0.05	70	1.4×10^6	0.05	87	1.7×10^6
3	$(Cd_{90}\text{-}Pb_{10})S$	0.1	37	3.7×10^5	0.1	40	4×10^5	0.1	43	4.3×10^5
4	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$	0.05	253	5.06×10^6	0.05	267	5.34×10^6	0.02	273	1.36×10^7
5	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$, La, Pr	0.05	297	5.94×10^6	0.05	308	6.16×10^6	0.02	311	1.55×10^7
6	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$, Pr	0.05	309	6.18×10^6	0.05	321	6.42×10^6	0.02	318	1.59×10^7
7	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$, La, Pr	0.05	321	6.42×10^6	0.05	326	6.52×10^6	0.02	335	1.67×10^7
8	$(Cd_{90}\text{-}Zn_{10})S$	0.1	72	3.6×10^5	0.1	80	8×10^5	0.1	87	8.7×10^5
9	$(Cd_{80}\text{-}Zn_{20})S$	0.1	90	9×10^5	0.05	98	1.96×10^6	0.05	103	2.06×10^6
10	$(Cd_{70}\text{-}Zn_{10})S$	0.05	23	2.3×10^5	0.05	43	8.6×10^5	0.05	69	1.38×10^6
11	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$	0.05	203	4.06×10^6	0.05	210	4.2×10^6	0.05	230	4.6×10^6
12	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$, La	0.05	272	5.44×10^6	0.05	280	5.6×10^6	0.05	295	5.9×10^6
13	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$, Pr	0.05	277	5.54×10^6	0.05	283	5.66×10^6	0.05	299	5.98×10^6
14	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$, La, Pr	0.05	288	5.76×10^6	0.05	290	5.8×10^6	0.05	320	6.4×10^6

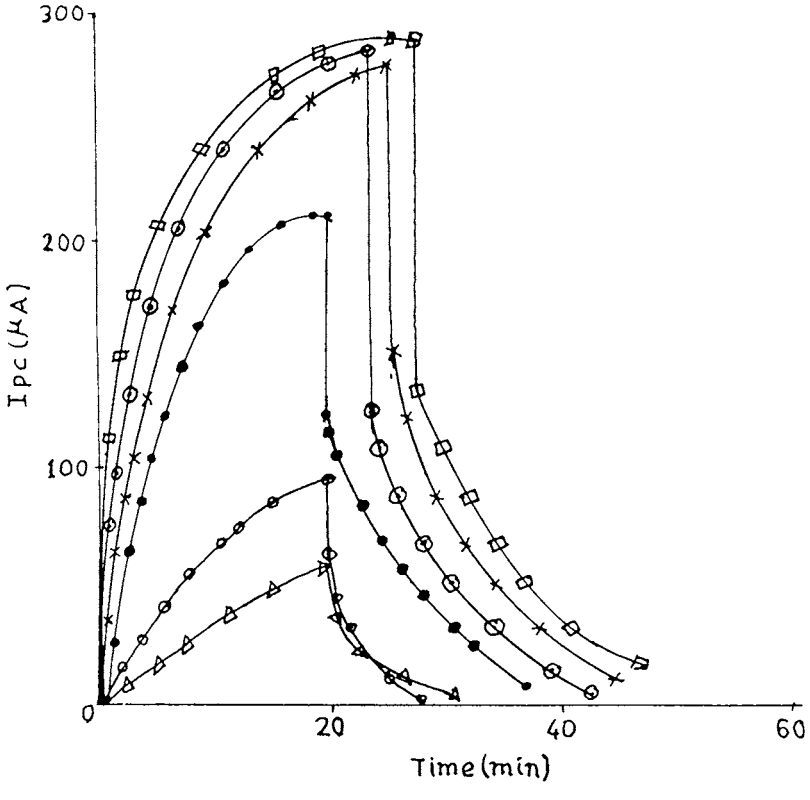

Figure 3 Rise and decay curves of different (Cd-Zn)S films. 1. (Δ) CdS; 2. (°) $(Cd_{80}\text{-}Zn_{20})S$; 3. (●) $(Cd_{80}\text{-}Zn_{20})S:CdCl_2$; 4. (x) $(Cd_{80}\text{-}Zn_{20})S:CdCl_2$, La; 5. (⊘) $(Cd_{80}\text{-}Zn_{20})S:CdCl_2$,Pr; 6. (□) $(Cd_{80}\text{-}Zn_{20})S:CdCl_2$La, Pr.

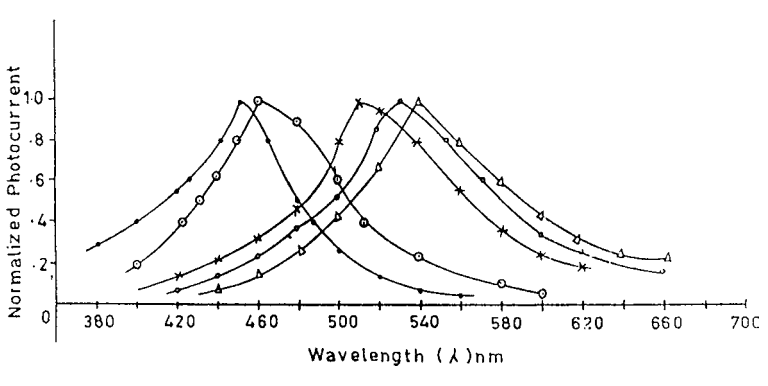

Figure 4 PC excitation spectra of different (Cd-Pb)S and (Cd-Zn)S films. 1. (x) CdS; 2. (°) $(Cd_{95}\text{-}Pb_{05})S$; 3. (Δ) $(Cd_{90}\text{-}Pb_{10})S$; 4. (⊘) $(Cd_{90}\text{-}Zn_{10})S$., 5. (●) $(Cd_{80}\text{-}Zn_{20})S$.

TABLE II Values of Life time and mobility in different (Cd -Pb)S and (Cd -Zn)S films

S. no.	System	Life time (s)	Mobility cm^2/V (s)	Trap parameters			
				p		E (eV)	
				p_1	p_2	E_1	E_2
01	$(Cd_{95}\text{-}Pb_{05})S$	30.04	47.50	.2526	.1892	.698	.705
02	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$	71.75	106.6	.1911	.1585	.704	.709
03	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$, La	73.3	112.01	.006	.0733	.795	.730
04	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$, Pr	74.65	114.67	.056	.090	.737	.727
05	$(Cd_{95}\text{-}Pb_{05})S:CdCl_2$ La, Pr	74.95	115.94	.048	.073	.740	.730
06	$(Cd_{80}\text{-}Zn_{20})$ S	42.06	62.22	.1036	.1308	.721	.715
07	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$	56	100	.1105	.1037	.719	.719
08	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$, La	70	106	.097	.090	.722	.724
09	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$, Pr	70.75	106.66	0.081	.1155	.727	.718
10	$(Cd_{80}\text{-}Zn_{20})S:CdCl_2$ La, Pr	73.41	105.35	0.064	.075	.733	.724

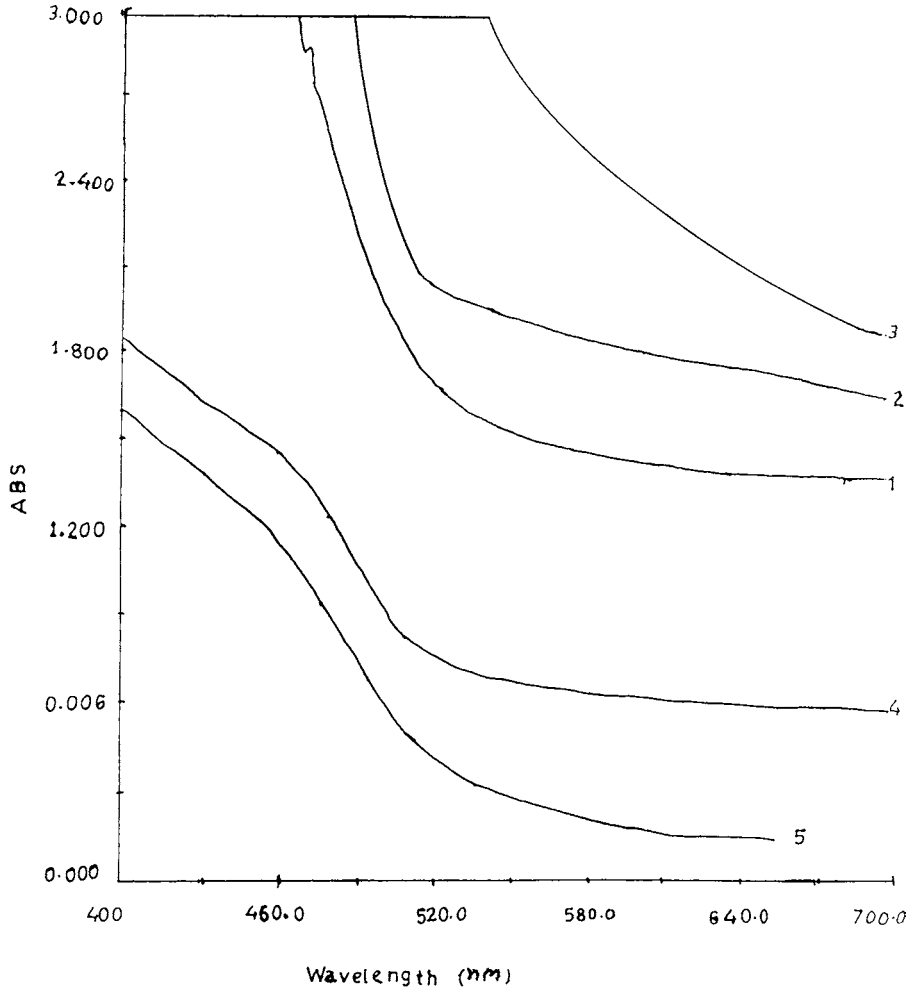

Figure 5 Optical absorption spectra of different films. 1. CdS, 2. $(Cd_{95}\text{-}Pb_{05})S$, 3. $(Cd_{90}\text{-}Pb_{10})$, 4. $(Cd_{90}\text{-}Zn_{10})S$, and 5. $(Cd_{80}\text{-}Zn_{20})S$.

to addition of Zn the rise and decay both become faster which is slowed down due to addition of impurities. The values of the ratio I_{pc}/I_{dc} observed for (Cd-Zn)S with NaF flux reported earlier [3] were of the order of 10^6 whereas in presence of $CdCl_2$ it improves to 10^7. It was reported earlier [9] that the NaF acted as flux and in its absence the substitution of Lanthanides was not possible. Karanjai and Dasgupta [10] found that CdS grains have a greater tendency to coalesce with the increase in concentration of $CdCl_2{\cdot}CdCl_2$ is known to promote crystallization of CdS [11].

It was also found that addition of ZnS affects the crystallinity i.e., the intensities of peaks in X-rays diffractograms reduces due to increase in concentration of ZnS [3]. A similar situation was reported by Karnajai and Dasgupta [10] alongwith complete amorphous nature of ZnS films. Further it was found that the SEM micrographs consisted of cabbage type structure [3] which showed layered growth of materials which finally resulted in cabbage. In earlier publication [12], it was reported that in the XRD pattern of (Cd-Pb)S films both cubic and hexagonal phases of CdS were present

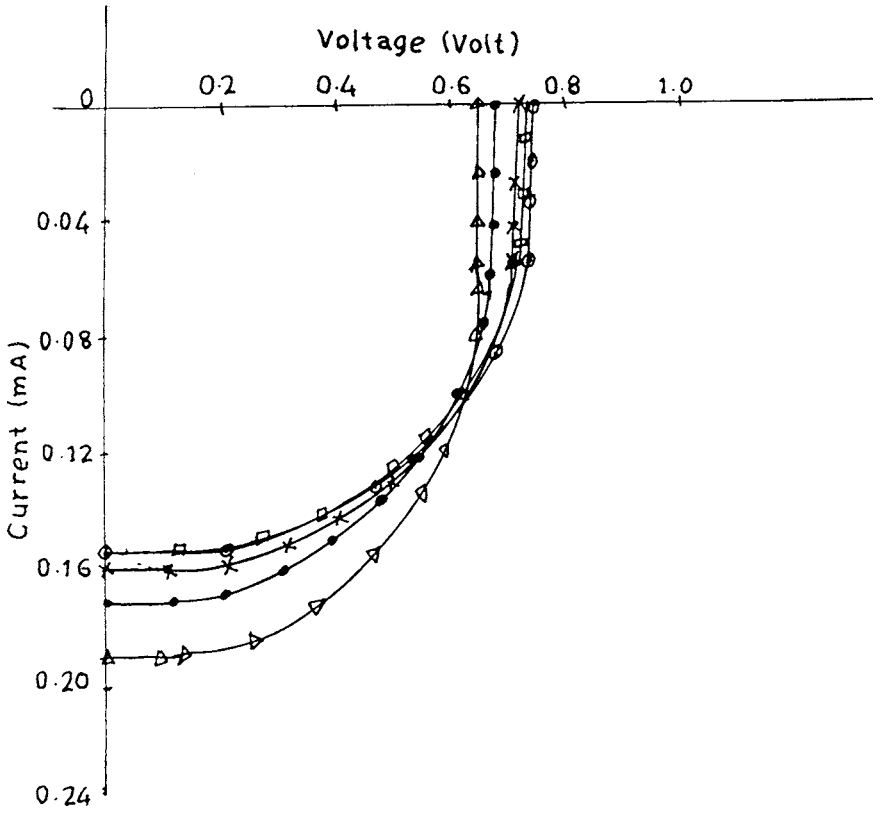

Figure 6 I-V Characteristics of different (Cd-Pb)S films. 1. (Δ) $(Cd_{95}\text{-}Pb_{05})S$; 2. (●) $(Cd_{95}\text{-}Pb_{05})S{:}CdCl_2$; 3. (x) $(Cd_{95}\text{-}Pb_{05})S{:}CdCl_2La$; 4. (⊘) $(Cd_{95}\text{-}Pb_{05})S{:}CdCl_2$,Pr, 5. (□) $(Cd_{95}\text{-}Pb_{05})S{:}\ CdCl_2$, La, Pr.

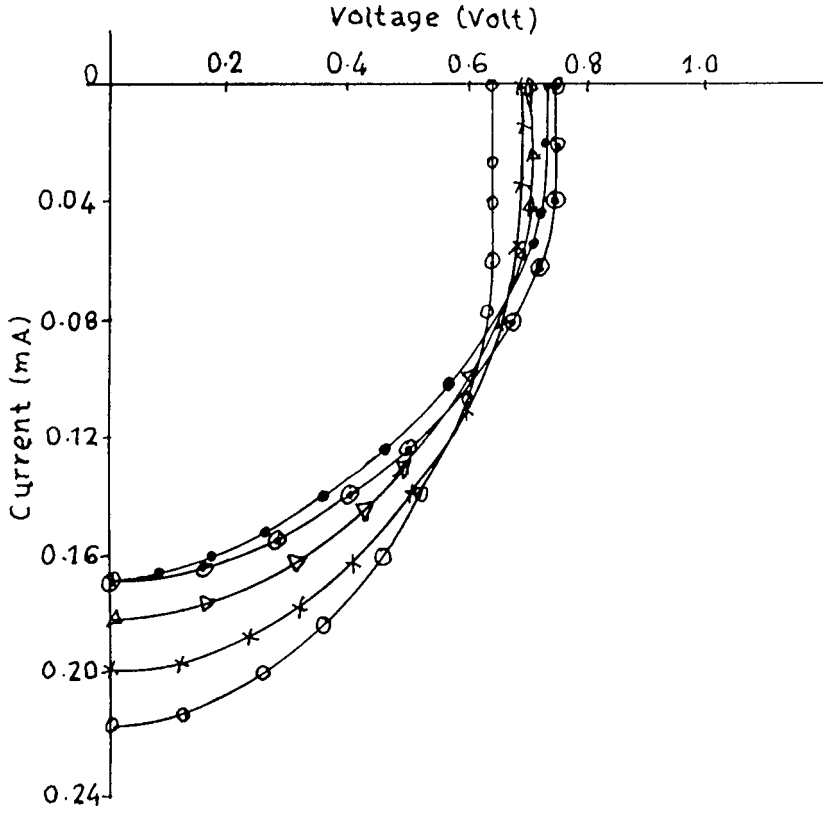

Figure 7 I-V Characteristics of different (Cd-Zn)S films 1. (°) $(Cd_{80}\text{-}Zn_{20})S$; 2. (x) $(Cd_{80}\text{-}Zn_{20})S\ CdCl_2$; 3. (Δ) $(Cd_{80}\text{-}Zn_{20})S{:}\ CdCl_2$, La; 4. (⊘) $(Cd_{80}\text{-}Zn_{20})S{:}CdCl_2$,Pr; 5. (●) $(Cd_{80}\text{-}Zn_{20})S{:}CdCl_2$, La, Pr.

alongwith diffraction lines of PbS. The SEM micrograph of this system again showed the presence of the layered growth with more favorable condition for such growth in presence of $CdCl_2$. Shikalgar and Pawar [13] found CdS films to be polycrystalline and contained 90% β cubic and 10% hexagonal forms. The electrical resistivity was found to be decreased with the increase in composition parameter x in $(CdS)_x\ (PbS\ )_{1-X}$ upto

0.5 and then increased for further increase in x [14]. Further, in films of [$Cd_{.7}$-$Zn_{.3}$) doped with indium from .01–5 mol%, the electrical conductivity was increased upto .1 mol% (10^9–10^4 Ωcm^{-1}).

Values of instantaneous lifetime, mobility and trap depth were evaluated by a method explained earlier [4]. The instantaneous values of lifetime can be determined from the initial state of PC decay using the relation

$$\tau = \Delta\sigma st/(d\sigma/dt)_{t=0} = \Delta\sigma st/\tan\delta \quad (1)$$

where σst is static photocurrent and tan δ is the slope of the initial state of the decay curves. The mobility was calculated using the relation

$$G = \tau\mu V/L^2 \quad (2)$$

where G is the PC photoconductivity gain, V is the applied voltage and L is the electrode spacing and corresponding values are presented in Table II. It is noticed that the lifetime and mobility both improve in presence of impurities. Maximum values are obtained corresponding to the concentration at which the maximum I_{pc}/I_{dc} ratio is obtained. This may be a reason for high photosensitization.

3.2. PC excitation spectra

The PC excitation spectra of different (Cd-Pb)S and (Cd-Zn)S films are shown in Fig. 4. The band gaps thus obtained are summarized in Table III. As expected, due to the addition of PbS band gap is found to decrease and that due to addition of Zn it is increased.

TABLE III Values of band gap energies for different (Cd-Pb)S and (Cd-Zn)S films

S. no.	System	Eg-from excitation spectra in (eV)	Eg-from optical absorption spectra (eV)
01	CdS	2.42	2.41
02	(Cd_{95}-Pb_{05})S	2.32	2.35
03	(Cd_{90}-Pb_{10})S	2.30	2.31
04	(Cd_{90}-Zn_{10})S	2.72	2.70
05	(Cd_{80}-Zn_{20})S	2.76	2.74

3.3. Optical absorption spectra

The results of optical absorption spectra for different systems are shown in Fig. 5. Values of band gaps were obtained from the plots of $(\alpha h\upsilon)^2$ vs $h\upsilon$. These values are also listed in Table III. It is found that mixing of both PbS & ZnS to CdS result in direct band gap material. A reduction in band gap occurs due to in corporation of PbS & increase in band gap results due to in corporation of ZnS. These results suggested formation of mixed lattice (Cd-Pb)S & (Cd-Zn)S also.

3.4. PV effect

The PV measurements were made for (Cd-Pb)S and (Cd-Zn)S films using conducting glass plate as one electrode and colloidal silver paste as the other electrode. Thus, it can behave as M-S contact. The corresponding I-V curves for different such systems are shown in Figs 6 and 7 respectively. The values of short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor [$I_m \times V_m/I_{sc} \times V_{oc}$ where I_m and V_m are the values corresponding to maximum power rectangle] and the efficiency [$\eta = [I_m \times V_m/P_{in}$, where P_{in} is input power = 2 mW] are summarized in Table IV. It is found that values of efficiency are found to vary between 3.12 to 3.71% and 3.24 to 3.64% for (Cd-Pb)S and (Cd-Zn)S films respectively. Such efficiency values are not low in view of the simplicity of the preparational method. Further, anti reflection coating can also improve the efficiency. Such work is going on. It is also observed that due to presence of impurities I_{pc}/I_{dc}, increases whereas the efficiency of PV effect decreases. It should be noted that the PC is a majority carrier phenomenon where as the PV effect is minority carrier phenomenon. The former is thus found to improve in presence of impurities. Lokhande & Pawar [15] used CdS films prepared by bath deposition in CuI_nGaSe_2, solar cells as a buffer layer. By using a bath composition 20 ml (0.2 M) $CdCl_2$ + 20 ml (7 M) NH_4OH + 5 ml (2.5 M) NH_4Cl + 40 ml (1 M) $CS(NH_2)_2$ and immersing the samples in ion exchange solution containing 200 ml (0.025M) thiosulphate + complex of $AgNO_3$ (pH = 7; immersion −20–30 S, heated at 150°C for 24 h) Ristova and Ristov [16] found that considerable enhancement was observed in photovoltaic cell parameters of SnO_2/CdS:Ag/SnS_xC cells.

4. Conclusions

Quite highly photosensitive materials can be prepared by a simple technique of chemical deposition of

TABLE IV Parameters of Photovoltaic studies for different (Cd-Pb)S & (Cd-Zn)S films

S. no.	System	$I_{sc(mA)}$	$V_{oc(V)}$	$I_{m(mA)}$	$V_{m(V)}$	F.F.	η (%)
01	(Cd_{95}-Pb_{05})S	0.19	0.65	0.14	0.53	0.60	3.71
02	(Cd_{95}-Pb_{05})S:$CdCl_2$	0.17	0.68	0.14	0.50	0.60	3.50
03	(Cd_{95}-Pb_{05})S:$CdCl_2$, La	0.16	0.72	0.13	0.52	0.58	3.38
04	(Cd_{95}-Pb_{05})S:$CdCl_2$, Pr	0.15	0.74	0.13	0.48	0.56	3.12
05	(Cd_{95}-Pb_{05})S:$CdCl_2$, La, Pr	0.14	0.73	0.12	0.55	0.64	3.30
06	(Cd_{80}-Zn_{20})S	0.22	0.65	0.14	0.52	0.50	3.64
07	(Cd_{80}-Zn_{20})S:$CdCl_2$	0.20	0.68	0.14	0.50	0.51	3.5
08	(Cd_{80}-Zn_{20})S:$CdCl_2$, La	0.18	0.70	0.13	0.53	0.54	3.44
09	(Cd_{80}-Zn_{20})S:$CdCl_2$, Pr	0.17	0.75	0.12	0.54	0.51	3.24
10	(Cd_{80}-Zn_{20})S:$CdCl_2$, La, Pr	0.17	0.73	0.12	0.525	0.50	3.15

(Cd-Pb)S and (Cd-Zn)S films. Highest values of I_{pc}/I_{dc} of the order of 10^7 have been achieved Photovoltaic efficiency of the order of about 3.12–3.71% has also been obtained from such films.

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