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Abstract

Stability effects in photoconductivity (PC) rise and decay have been studied over a period of 2 years in thin films of (Cd-Pb)S:LiF, La/Pr and (Cd-Zn)S: LiF,La/Pr and have been found quite stable; however, those of CdS are not that stable. Results of annealing effect are also included, which present more stable values. XRD studies show prominent lines of base materials. Further, XRD and SEM studies show the particle sizes are in the nanometer range. Results of optical absorption spectra have been used to evaluate the band gap of the materials. Effect of thickness of the Ag electrode has also been included.

Key Words: Photoconductivity, chemical deposition, and stability effect.

1. Introduction

Photoconductivity (PC) studies of II-VI compounds are quite important due to their broad applications in Xerography, photovoltaic solar energy conversion and thin film transistor electronics. Chemical deposition has been found to be quite useful since it presents low cost technique and has been attempted by a number of workers [1, 2, 3]. Bhushan et al [4, 5, 6] reported the photocurrent to dark-current ratio $\sim 10^7$ along with photovoltaic effect [7, 8] with a maximum efficiency of 3.71% in (Cd-Zn)S films. The importance of such high photoresponse can be of technological value only when the responses are stable over longer duration. With this aim, stability in PC response was studied for a period of 2 years on CdS, (Cd-Pb)S and (Cd-Zn)S films and the results of this study are presented in this paper. Along with these studies, results of XRD, SEM and absorption spectra are also presented in this paper. Results of effect of thickness of Ag electrode are also discussed.

2. Experimental Details

Film deposition was produced by precipitation followed by condensation on glass substrates. The various chemicals used were 1 M of cadmium acetate / zinc acetate/ lead acetate, thiourea, triethanolamine, aqueous ammonium hydroxide and 0.01 M LiF and La and Pr. The films were prepared at a constant temperature of 60 °C in water bath for 1 hour. The photoconductivity excitation source was an incandescent bulb of

100 W (net illumination power = 18 mW). For PC studies co-planar electrodes of colloidal silver (1.5 mm wide, 24 mm long, with a separation of 2 mm) were painted and dried on the surface of the films. The photocurrents were measured using a DNM-121 nanoammeter at a applied voltage of 15 V. The films were preserved in a desiccator and the PC studies were made at different durations. XRD and SEM studies were preformed at Delhi University and absorption spectral studies were made using a Varian spectrophotometer. Since thickness estimation of the colloidal silver electrodes was difficult to measure accurately, to study its effect on PC, Ag electrodes of different thicknesses were deposited on the film by using a vacuum coating unit [12 inch Hind-HiVac (12A4D)] at a pressure of 10^{-5} torr.

3. Results and Discussion

The results of PC rise and decay curves for unannealed films of CdS; $(Cd_{.95}\text{-}Pb_{.05})S$; $(Cd_{.95}\text{-}Pb_{.05})S$: LiF; $(Cd_{.95}\text{-}Pb_{.05})S$: LiF, La; $(Cd_{.95}\text{-}Pb_{.05})S$: LiF, Pr and $(Cd_{.95}\text{-}Pb_{.05})S$: LiF, La, Pr are shown in Figures 1 and 2 under instantaneous condition and after 24 months of aging, respectively.

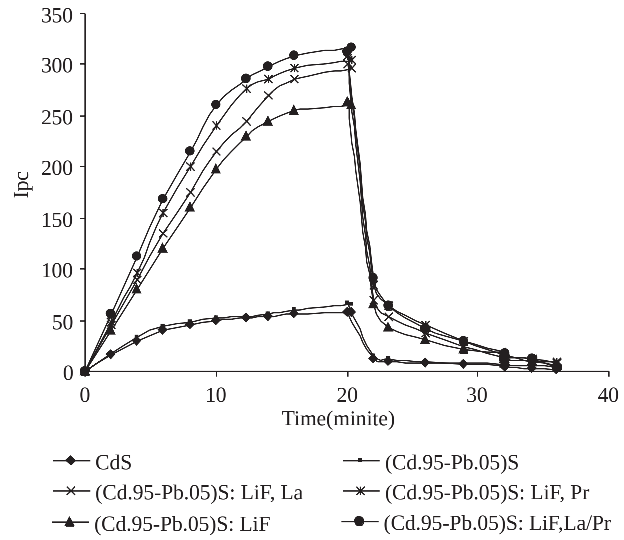

Figure 1. Rise and decay curves of different CdS & (Cd-Pb)S Films under instantaneous condition.

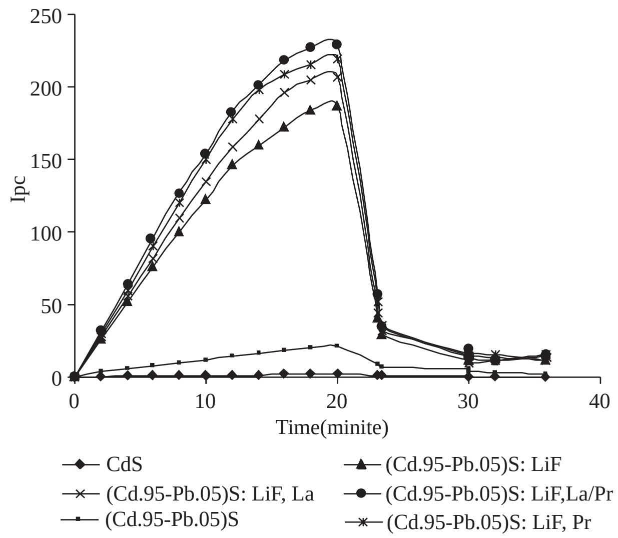

Figure 2. Rise and decay curves of different CdS & (Cd-Pb)S Films after 24 months.

Similarly the results of rise and decay curves for different unannealed (Cd-Zn)S films under the instantaneous conditions and after 24 months of preparation are shown in Figures 3 and 4, respectively.

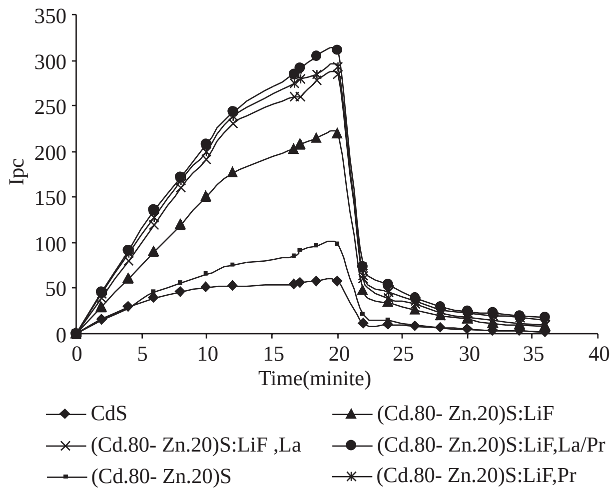

Figure 3. Rise and decay curves of different CdS & (Cd-Pb)S films under instantaneous condition.

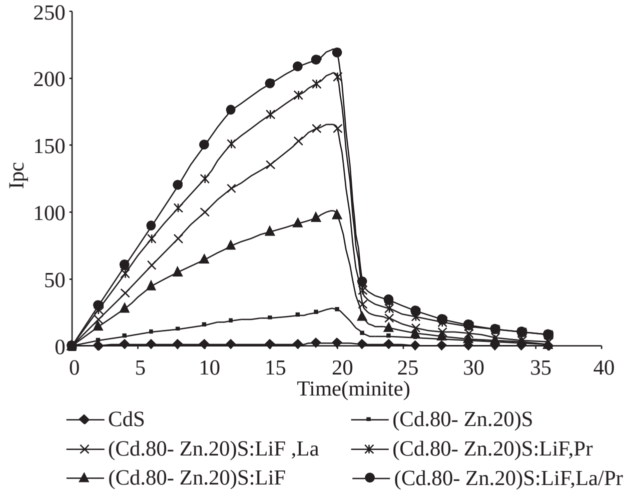

Figure 4. Rise and decay curves of different CdS & (Cd-Pb)S films after 24 months.

Due to annealing, the photocurrent and the ratio of photo to dark current both improve. The nature of rise and decay curves in doped (Cd-Pb)S and (Cd-Zn)S films appear to be similar to those observed for instantaneous films. However, there is change in the nature of such studies for undoped CdS, (Cd-Pb)S and (Cd-Zn)S films. Value of I_{dc}, I_{pc} and then I_{dc}/I_{dc} observed over a period of 2 years are presented in Tables 1 and 2 for unannealed and annealed films respectively.

Table 1. Values of dark current (I_{dc}), photocurrent (I_{pc}) and the ratio of (I_{pc}/I_{dc}) for different (Cd-Pb)S and (Cd-Zn)S films (Temperature of deposition =60 °C, Time of deposition =1 hour , Voltage = 15 Volts) studied over a period of 24 months.

Sample Number	System	0 month			6 month			12 month			18 month			24 month		
		I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}
1	CdS	0.2	58	2.9×10^5	0.3	43	1.43×10^5	0.3	18	6.0×10^4	0.5	3	8×10^3	.5	1.61	3.22×10^3
2	$(Cd_{.95}$-$Pb_{.05})S$	0.05	67	1.34×10^6	0.05	60	1.2×10^6	0.07	53	7.57×10^5	0.08	36	4.5×10^5	0.09	21	2.33×10^5
3	$(Cd_{.95}$-$Pb_{.05})S$: LiF	0.05	263	5.34×10^6	0.05	259	5.18×10^6	0.05	241	4.82×10^6	0.06	209	3.48×10^6	0.07	187	2.67×10^6
4	$(Cd_{.95}$-$Pb_{.05})S$: LiF, La	0.05	301	6.02×10^6	0.05	298	5.96×10^6	0.05	383	5.66×10^6	0.06	249	4.15×10^6	0.07	207	2.95×10^6
5	$(Cd_{.95}$-$Pb_{.05})S$: LiF, Pr	0.05	308	6.16×10^6	0.05	301	6.02×10^6	0.05	258	5.7×10^6	0.06	260	4.2×10^6	0.07	219	3.12×10^6
6	$(Cd_{.95}$-$Pb_{.05})S$: LiF,La/Pr	0.05	312	6.24×10^6	0.05	306	6.12×10^6	0.05	290	5.8×10^6	0.06	270	4.5×10^6	0.07	229	3.27×10^6
7	$(Cd_{.80}$- $Zn_{.20})S$	0.1	90	9×10^5	0.1	86	8.6×10^5	0.2	71	3.55×10^5	0.2	46	2.3×10^5	0.3	27	9×10^4
8	$(Cd_{.80}$- $Zn_{.20})S$: LiF,	0.05	209	4.18×10^6	0.05	193	3.86×10^6	0.05	166	3.32×10^6	0.06	129	2.15×10^6	0.07	98	1.4×10^6
9	$(Cd_{.80}$- $Zn_{.20})S$: LiF, La	0.05	255	5.1×10^6	0.05	249	4.98×10^6	0.05	207	4.14×10^6	0.06	193	3.12×10^6	0.07	163	2.32×10^6
10	$(Cd_{.80}$- $Zn_{.20})S$: LiF, Pr	0.05	279	5.58×10^6	0.05	270	5.4×10^6	0.05	251	5.02×10^6	0.06	227	3.78×10^6	0.07	201	2.87×10^6
11	$(Cd_{.80}$- $Zn_{.20})S$: LiF La/Pr	0.05	289	5.6×10^6	0.05	280	5.6×10^6	0.05	257	5.14×10^6	0.06	248	4.13×10^6	0.07	219	3.12×10^6

Table 2. Values of dark current (I_{dc}), photocurrent (I_{pc}) and the ratio of (I_{pc}/I_{dc}) for different (Cd-Pb)S and (Cd-Zn)S films (Temperature of deposition =60 °C, Time of deposition =1 hour, Voltage = 15 Volts) studied over a period of 24 months.

Sample Number	System	0 month			6 month			12 month			18 month			24 month		
		I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}	I_{dc}	I_{pc}	I_{pc}/I_{dc}
1	CdS	0.1	60	6×10^5	0.1	58	5.8×10^5	0.2	43	6.0×10^5	0.3	29	9.6×10^4	0.3	10	$3..3\times10^4$
2	$(Cd_{.95}$-$Pb_{.05})S$	0.05	70	$1..4\times10^6$	0.05	70	1.4×10^6	0.06	57	9.5×10^5	0.07	37	5.28×10^5	0.08	21	3.62×10^5
3	$(Cd_{.95}$-$Pb_{.05})S$: LiF	0.01	276	2.76×10^7	0.01	276	2.76×10^7	0.01	253	2.53×10^7	0.02	235	1.17×10^7	0.03	219	7.3×10^6
4	$(Cd_{.95}$-$Pb_{.05})S$: LiF, La	0.01	327	3.27×10^7	0.01	327	3.27×10^7	0.01	309	3.09×10^7	0.02	286	1.43×10^7	0.03	270	1.35×10^7
5	$(Cd_{.95}$-$Pb_{.05})S$: LiF, Pr	0.01	341	3.41×10^7	0.01	341	3.41×10^7	0.01	329	3.29×10^7	0.02	311	1.55×10^7	0.03	287	1.43×10^7
6	$(Cd_{.95}$-$Pb_{.05})S$: LiF,La/Pr	0.01	343	3.43×10^7	0.01	343	3.43×10^7	0.01	331	1.06×10^6	0.02	313	4.5×10^7	0.02	290	1.45×10^7
7	$(Cd_{.80}$- $Zn_{.20})S$	0.05	98	9×10^6	0.05	98	9×10^6	0.06	73	3.55×10^5	0.07	52	7.42×10^5	0.07	41	5.85×10^5
8	$(Cd_{.80}$- $Zn_{.20})S$: LiF,	0.01	218	2.18×10^7	0.01	218	2.18×10^7	0.01	203	2.03×10^7	0.02	182	9.1×10^7	0.03	159	5.3×10^6
9	$(Cd_{.80}$- $Zn_{.20})S$: LiF, La	0.01	284	2.84×10^7	0.01	284	2.84×10^7	0.01	271	2.71×10^7	0.02	250	1.25×10^7	0.03	226	7.5×10^6
10	$(Cd_{.80}$- $Zn_{.20})S$: LiF, Pr	0.01	292	2.92×10^7	0.01	292	2.92×10^7	0.01	275	2.75×10^7	0.02	256	1.28×10^7	0.03	231	7.9×10^6
11	$(Cd_{.80}$- $Zn_{.20})S$: LiF La/Pr	0.01	310	3.1×10^7	0.01	310	3.1×10^7	0.01	291	2.91×10^7	0.02	264	1.32×10^7	0.02	239	1.19×10^7

Variation of I_{pc}/I_{dc} ratio with time are presented in Figures 5, 6, 7 and 8 for unannealed and annealed (Cd-Pb)S and (Cd-Zn)S films. These figures also show that in the presence of lanthanides, used in the present investigation, the behavior of I_{pc}/I_{dc} are quite stable.

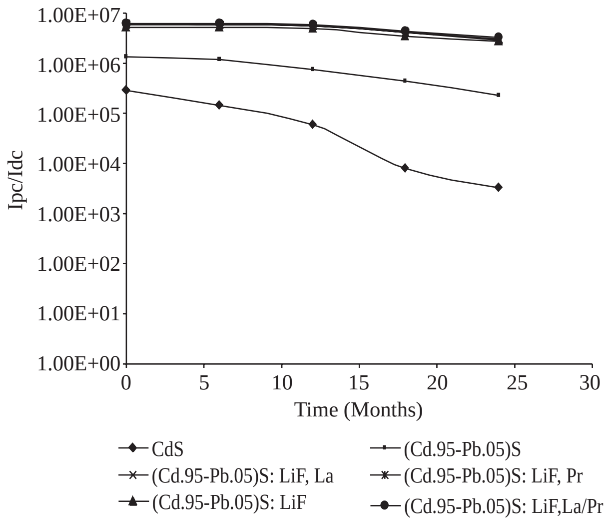

Figure 5. Variation of Ipc/Idc ratio with time for unannealed (Cd-Pb)S Films.

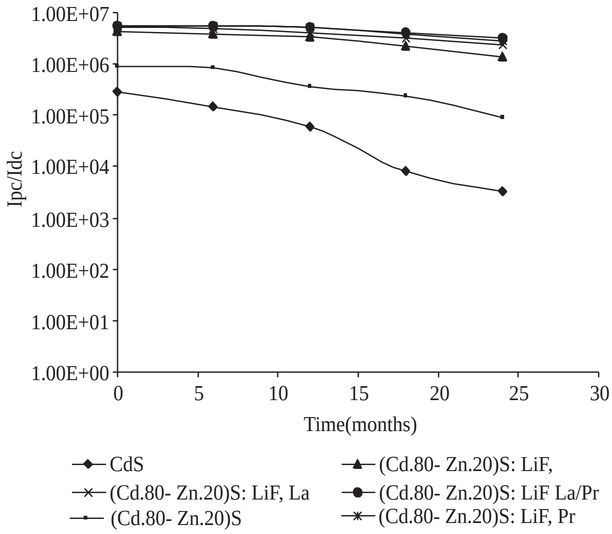

Figure 6. Variation of Ipc/Idc ratio with time for unannealed (Cd-Zn)S films.

The optical absorption spectra for $(Cd_{0.80}\text{-}Zn_{0.20})S$: LiF under annealed and unannealed conditions are shown in Figure 9. From $(\alpha h\nu)^2$ vs. $h\nu$ plots (Tauc's plots) the band gaps were found to be 2.72 eV and 2.70 eV, respectively. The nature of band gaps was of direct type.

XRD diffractogram of $(Cd_{0.80}\text{-}Zn_{0.20})S$: LiF is shown in Figure 10. The assignment of peaks was made by comparing with ASTM data and also through evaluation of lattice constants. All these values are presented in Table 3. It is found that prominent lines of CdS alongwith some lines of ZnS appear in the diffractograms.

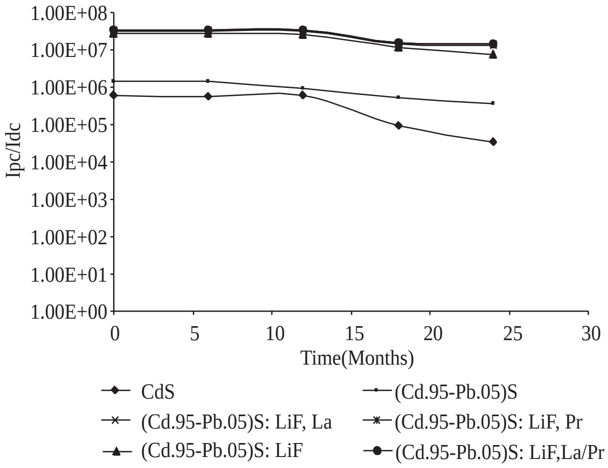

Figure 7. Variation of Ipc/Idc ratio with time for annealed (Cd-Pb)S films.

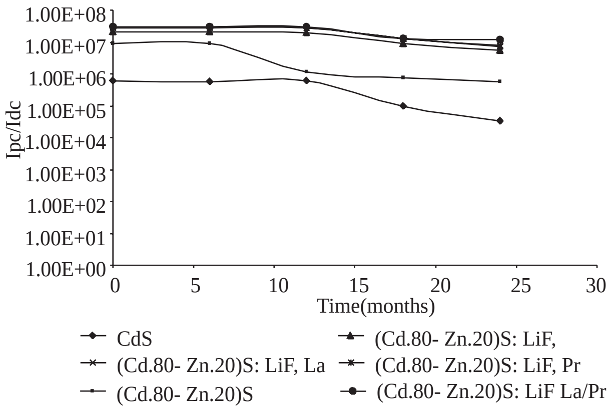

Figure 8. Variation of Ipc/Idc ratio with time for annealed (Cd-Zn)S Films.

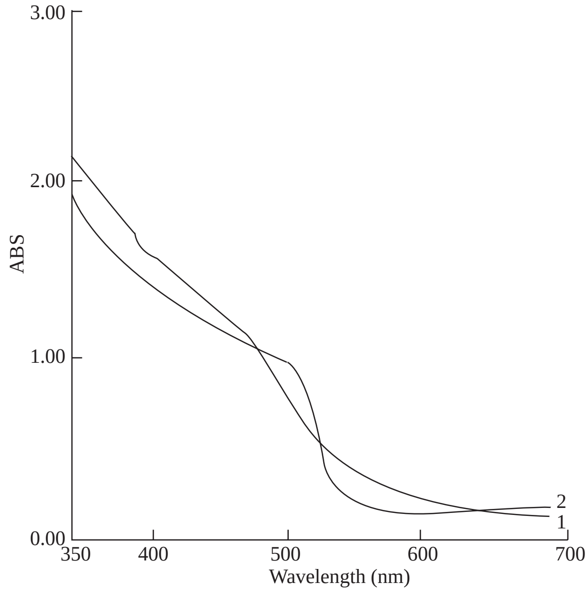

Figure 9. Optical absorption spectra of $(Cd_{0.80}-Zn_{0.20})S$: LiF films under (1) Annealed and (2) Unannealed Conditions.

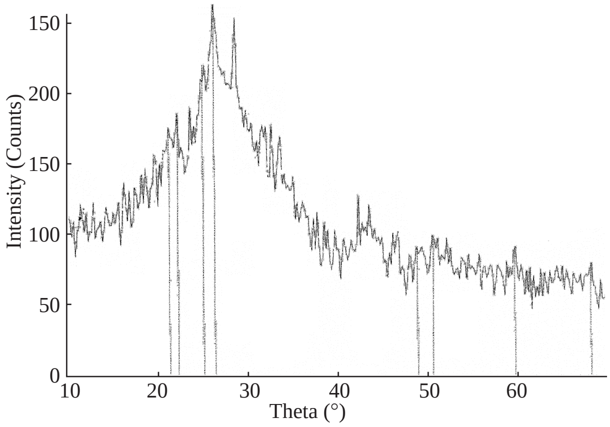

Figure 10. X-ray diffractograms of $(Cd_{0.80} - Zn_{0.20})S$: LiF Films.

Table 3. XRD data of $(Cd_{.80}\text{-}Zn_{.20})S$: LiF film. (Temperature of deposition = 60 °C, Time of deposition = 1 hour)

d-values (Å)		Relative intensities		h k l	Lattice constant (Å)		Average particle
Obs.	Rep.	Obs.	Rep.		Obs.	Rep.	size (Å)
3.5311	M m3.503	40	75	$(100)_h$CdS	4.07	4.135	3.67
3.3685	3.360	100	100	$(111)_c$CdS	5.834	5.818	2.75
1.9428	2.058	62	80	$(220)_c$ CdS	5.495	5.818	2.61
1.8601	1.912	40	51	$(220)_c$ ZnS	5.261	5.4060	1.63
1.7997	1.753	38	60	$(311)_c$ CdS	5.968	5.818	3.91
1.5472	1.561	46	2	$(222)_c$ ZnS	5.359	5.4060	3.34
1.3751	1.351	38	6	$(400)_c$ ZnS	5.48	5.4060	4.56

The particle sizes of the crystals were determined by using the formula [9]

$$D = K\lambda/(\beta_{1/2}\cos\theta), \tag{1}$$

where λ is the X-ray wavelength and θ the Bragg's angle (in radians), K is a constant, which depends on the grain shape (0.89 for circular grains), $\beta_{1/2}$is the full width at half-maximum (FWHM). It is found that particle sizes vary between 4.56 Å to 1.63 Å. The SEM micrograph of $(Cd_{.80}\text{-}Zn_{.20})S$: LiF is shown in Figure 11.

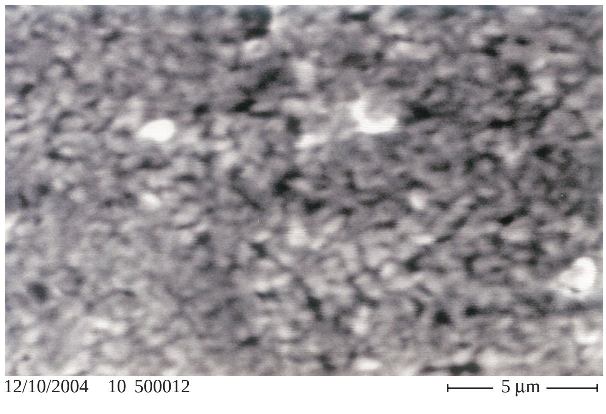

Figure 11. SEM micrographs of $(Cd_{.80}\text{-} Zn_{.20})S$: LiF film.

To investigate the effect of thickness of electrode of Ag in rise and decay curves, studies were made for a sample with varying thickness of Ag electrode. For such variation Ag electrode was deposited in vacuum coating unit. The thickness was varied from 2 kÅ to 10 kÅ. The thickness of colloidal silver paste used in all other films was of the order of 2 μm. The results of rise and decay curves under these conditions are shown in Figure 12. From these curves two important inferences are drawn: (1) the photocurrent increases with an increase in thickness of Ag electrode, (ii) the saturation time of photocurrent also increases. From this observation it inferred that Ag also contributes to photocurrent due to irradiation through slow release of electrons, which increases the photocurrent as well as the saturation time.

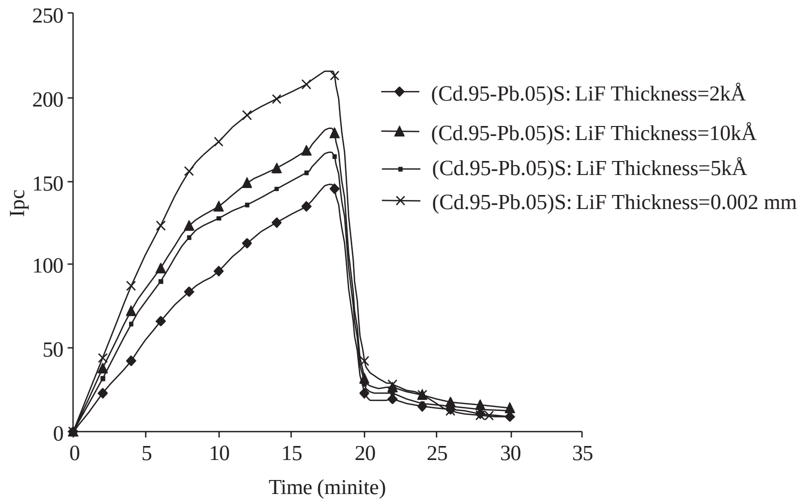

Figure 12. Rise and decay curve of (Cd-Zn)S: LiF films with different thicknesses of Ag electrode.

4. Conclusions

The photocurrent response of films prepared by chemical bath technique is found to be quite stable for (Cd-Pb)S and (Cd-Zn)S films over a period of 2 years. However, the photocurrent response of CdS is found to be comparatively less stable. The SEM and XRD studies show particle size in the nano range.

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