

Photoconductivity of chemically deposited lanthanum doped (Cd–Zn)S films

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Abstract : Photosensitive films with photocurrent to dark current ratios of the order of 10^5 have been prepared by doping (Cd–Zn)S with lanthanum. The conditions for preparing such films are described and results of rise and decay curves, excitation and transmission spectra, SEM and XRD studies are presented. Band gap values obtained from the two spectra are discussed in terms of the role of impurities and annealing effect *etc.* Values of trap depths, life time and mobility of charge carriers are determined.

Keywords : Photoconduction, (Cd–Zn)S films

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1. Introduction

Photoconductivity studies of sulphide films are important because of their technological applications in Xerography, Photovoltaic solar energy conversion and thin film transistors *etc.* A variety of methods like vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy [1] and chemical deposition *etc.* [2–4] have been used to prepare such films. Chemical deposition is one of the low cost techniques. Recently, at least a thousand-fold improvement in the Opto-electronic characteristics of solar assisted chemically deposited films have been reported by Nair *et al* [3,5]. Also, Bhushan and coworkers [4,6–8] have reported many fold improvement in the photoconductivity of CdS by doping with yttrium, lanthanum, dysprosium, neodymium and praseodymium. The present paper reports the results of photoconductivity studies of (Cd–Zn)S films by doping with lanthanum prepared by chemical deposition technique.

2. Experimental

For the deposition of the films, commercial quality microscopic glass slides of dimensions 24 mm × 75 mm were dipped in a mixture of solutions of appropriate volumes of 1 M

cadmium acetate, zinc acetate, thiourea, triethanolamine and 30% aqueous-ammonia (all analytical reagent grade). The pH value of this mixture was approximately in the range 10–11. For preparing the doped films, calculated proportions of 0.01 M solutions of NaF and lanthanum nitrate were mixed in the original mixture and then the depositions were made. The depositions were done at 74°C in a 'Tempo' constant temperature bath. No stirring was done during the process of deposition. After deposition, the films were cleaned by flushing with distilled water and then dried by keeping the plates in open atmosphere at room temperature. The film thickness of $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S}$ was measured by weight difference method and was found to vary from 0.985 μm to 2.963 μm for dipping times between 30 min to 1.5 hours.

For photoconductivity studies, co-planar silver paint electrodes (2 mm wide and 24 mm long) were attached to the surface of the films at a separation of 2 mm. The excitation sources used for rise and decay and excitation spectral studies were commercial incandescent bulbs of 100 W and 1 KW respectively. The photocurrents were recorded by a nanometer (Scientific Equipment, Roorkee NM 122). The excitation spectra were studied by using a prism monochromator (As 17050 from M/s Andhra Scientific Co Machilipatanam) and the correction of spectra was done by a method published earlier [9]. For recording transmission spectra a Varian (UV-VIS) DMS-100 spectrophotometer was used.

3. Results and discussion

3.1. Rise and decay studies :

Figure 1 shows the rise and decay curves of unannealed films of $(\text{Cd}_{0.9}\text{Zn}_{0.1})\text{S}$ prepared at different dipping times at a bath temperature of 74°C. From this figure, it is clear that the photocurrent goes on increasing with increase in dipping time. The values of photo-to-dark current ratio (I_{PC}/I_{DC}) determined from saturated photocurrent for the films prepared at different dipping times are 2.1×10^4 (30 min; $I_{DC} = 0.1$ nA), 8.4×10^4 (45 min; $I_{DC} = 0.1$ nA), 5.9×10^5 (1 h; $I_{DC} = 0.1$ nA), 6.9×10^5 (1.25 h; $I_{DC} = 0.1$ nA) and 3×10^5 (1.5 h; $I_{DC} = 0.3$ nA). The ratio is found to be highest for 1.25 h dipping time and thus this dipping time was preferred for preparing the films. This happens because of increase in dark current at further higher dipping times. The rise and decay curves of different mixed base systems and the impurity doped systems were found to be similar in nature. The values of the ratio I_{PC}/I_{DC} for different systems were found as follows : $(\text{Cd}_{0.9}\text{Zn}_{0.1})\text{S} : 6.9 \times 10^5$, $(\text{Cd}_{0.8}\text{Zn}_{0.2})\text{S} : 4.4 \times 10^5$, $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S} : 2.6 \times 10^5$, $(\text{Cd}_{0.5}\text{Zn}_{0.5})\text{S} : 0.48 \times 10^5$, $(\text{Cd}_{0.3}\text{Zn}_{0.7})\text{S} : 0.26 \times 10^5$, $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S} : \text{NaF}$ (5.0 ml); 3.9×10^5 , (best value), $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S} : \text{NaF} : \text{La}$ (2.5 ml) : 1.62×10^6 , (best value). The ratio is found to decrease with increasing proportion of zinc. The band gap of ZnS is more as compared to that of CdS and therefore, with increasing proportion of Zn the excitation under visible radiation becomes less possible comparatively which results, in lowering of photocurrent. It was also found that the film was not formed properly with the increase in concentration of zinc content. Satisfactory films could only be obtained up to 30 : 70 ratio of cadmium to zinc. The 70 : 30 ratio of cadmium to zinc was

preferred for general studies because of satisfactorily high value of I_{PC}/I_{DC} and its band gap. The value of the ratio in the undoped system has been found to be higher compared to that

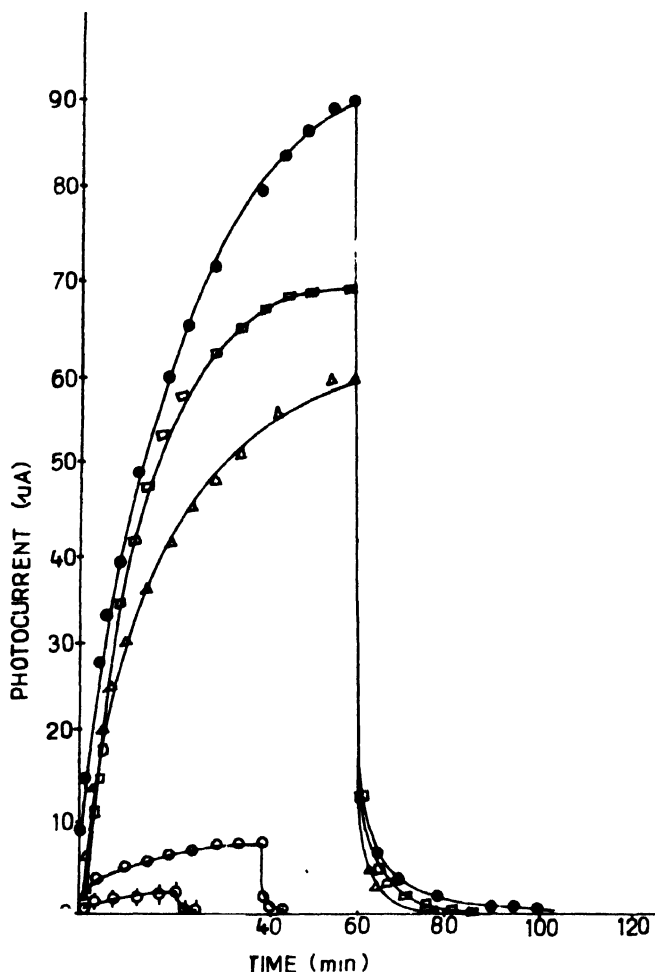


Figure 1. Rise and decay curves of different unannealed $(Cd_{0.9}Zn_{0.1})S$ films prepared at different dipping times (bath temperature $74^{\circ}C$), ϕ -30 min, \odot -45 min, Δ -1 h, \square -1.25 h, \bullet -1.5 h.

obtained for CdS by earlier workers at this place [6,8]. This may be due to the reason that samples in the present case were prepared at higher temperature ($74^{\circ}C$). Probably this results in anion vacancies and so due to action of light, the cations are ionized easily resulting in more current. The proportionate increase in presence of impurities is not high as compared to their observations although the total increase in the present case is higher. This may happen due to compensation effect of vacancies in presence of impurities.

Due to annealing of films at $400^{\circ}C$ in air, the highest value of the ratio I_{PC}/I_{DC} was found at 2 min of annealing. High photosensitivity in such compounds can be associated with the presence of compensated acceptors. In order to provide these compensated

dotted line is showing the linearity). A similar dependence has been reported in the literature earlier [19].

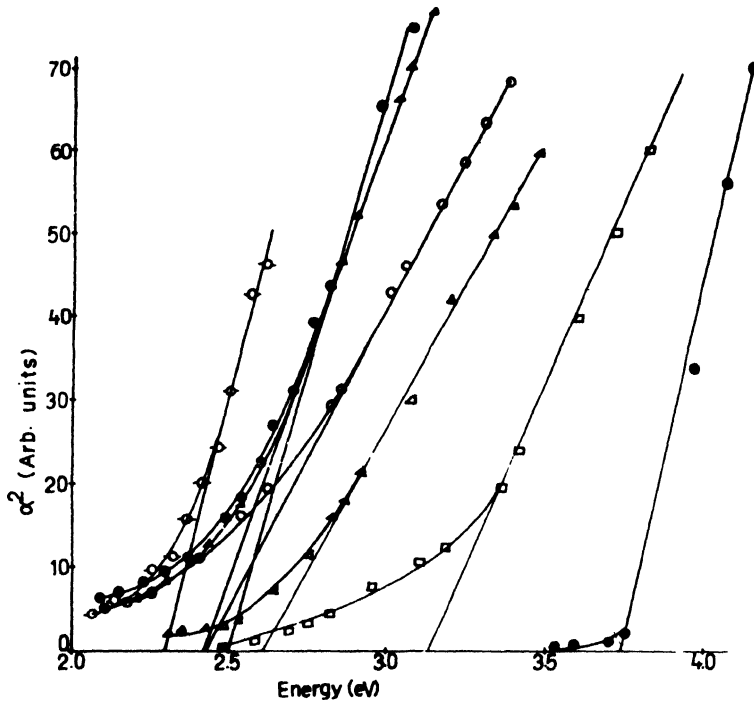


Figure 3. The plot of α^2 against energy ($h\nu$) for different unannealed films.

- — CdS,
- △ — $(\text{Cd}_{0.5}\text{Zn}_{0.5})\text{S}$,
- — ZnS,
- ▲ — $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S} : \text{NaF (5.0 ml), La (2.5 ml)}$,
- ⊗ — $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S}$,
- — $(\text{Cd}_{0.3}\text{Zn}_{0.7})\text{S}$,
- () — $(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S} \cdot \text{NaF (5.0 ml)}$.

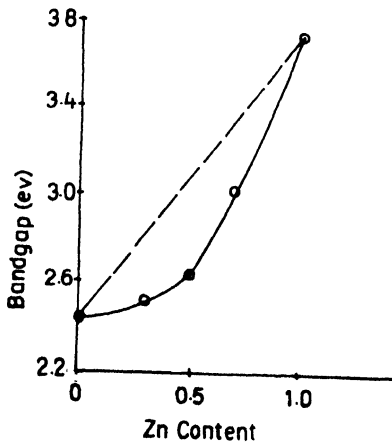


Figure 4. Dependence of band gap energy on Zn content in $(\text{Cd}_{1-x}\text{Zn}_x)\text{S}$ films.

Annealing effect produces certain changes in the transmission and the corresponding results are also included in Figure 2 (dotted lines). The plots of α^2 vs $h\nu$ for annealed films were found to be quite similar to those of unannealed films but the band gap values were found to be different. The band gap values are summarized in Table 1. It is found that the band gap decreases due to annealing. Also, due to incorporation of impurities NaF and

Table 1. Values of band gap energies for unannealed and annealed CdS and $(\text{Cd}_{1-x}\text{Zn}_x)\text{S}$ films (temp. of deposition 74°C and time of deposition 1.25 h).

Sl. No.	System	Conditions	Band gap energy (eV)	
			From excitation spectra	From transmission spectra
1	CdS	Unannealed	2.38–2.41	2.44
		Annealed	2.34	2.36
2	$(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S}$	Unannealed	2.48	2.50
		Annealed	2.36	2.33
3.	$(\text{Cd}_{0.5}\text{Zn}_{0.5})\text{S}$	Unannealed	2.64	2.62
		Annealed	2.50	2.52
4.	$(\text{Cd}_{0.3}\text{Zn}_{0.7})\text{S}$	Unannealed	2.69	3.14
		Annealed	2.48–2.50	2.98
5.	ZnS	Unannealed	—	3.74
		Annealed	—	3.72
6	$(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S}$ NaF (5.0 ml)	Unannealed	2.38–2.36	2.30
		Annealed	2.36–2.34	2.27
7.	$(\text{Cd}_{0.7}\text{Zn}_{0.3})\text{S}$: NaF (5.0 ml), Lanthanum nitrate (2.5 ml)	Unannealed	2.43–2.48	2.42
		Annealed	2.38	2.35

lanthanum, the transmission is again affected and corresponding results are also included in Figure 2. The α^2 vs $h\nu$ plots for this case are presented in Figure 3. The band gap values are mentioned in Table 1. In these cases also band gaps decrease slightly. The change in band gap is related to the size difference of the impurities as compared to those of host ions. Due to annealing more ions may be considered to be substituted which results in decrease in band gaps.

The excitation spectra of some selected films under annealed conditions are shown in Figure 5. The energy corresponding to the peak values are summarized in Table 1. The peak energies obtained from excitation spectral studies for different films except that of $(\text{Cd}_{0.3}\text{Zn}_{0.7})\text{S}$, are found to be quite close to those obtained from transmission spectral studies. From both studies, it is observed that due to annealing the band gap

Photoconductivity of chemically deposited lanthanum etc

Plate 1

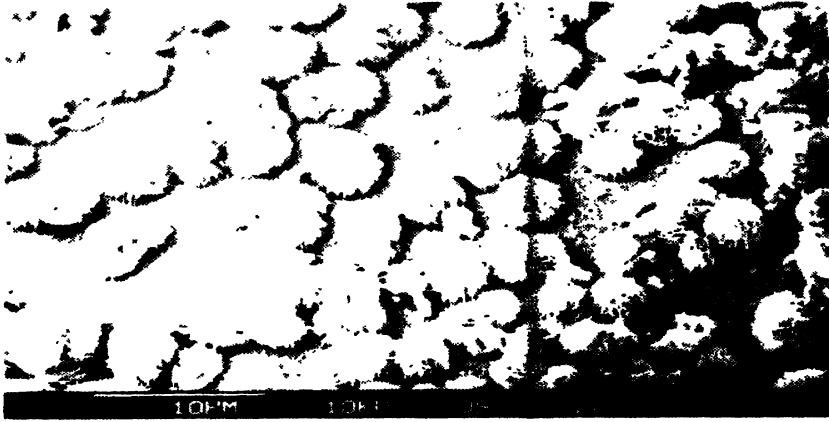


Figure 6. SEM micrographs of (Cd-Zn)S : NaF (5.0 ml), La (2.5 ml) at 2500x.

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