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CHARACTERIZATION AND OPTICAL STUDIES OF Sm^{3+} AND Dy^{3+} DOPED CHEMICALLY DEPOSITED CdS-Se FILMS

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Results of SEM and XRD studies, optical absorption spectra and photoluminescence (PL) emission studies are reported for Cd(S-Se):$CdCl_2$,Sm/Dy films prepared by chemical deposition method on glass substrates at 60^0C in a water bath (WB). SEM studies show ball type structure with voids which is related to layered growth. XRD studies show prominent diffraction lines of CdS and CdSe along with lines of $CdCl_2$ and Sm. The chemically deposited CdS-Se films are found to consist of two PL emission peaks, one at 494 nm and the other shifting from 516 nm to 577 nm with increasing concentration of Se. The peak at 494 nm may be attributed to the exciton bound to neutral donor levels formed by sulphur/excess Cd, and the other peak may be attributed to the radiative decay of the free exciton. The peak at 494 nm may also be due to the shift of bulk emission of CdS at 511 nm (nano-crystalline effect). In Sm doped films, three new peaks appear at 563, 595 and 614 nm (as compared to the PL spectra of base material), which may be related to the transitions in Sm-levels. In Dy doped films, two new peaks appear at 484 and 573 nm, which may be related to the transitions in Dy-levels..

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Keywords: Chemical bath deposition, X-ray diffraction, Energy band-gap and Photoluminescence

1. Introduction

CdS/CdSe are direct band gap semiconductors belonging to II-VI group. The wide technological applications of CdS type materials make the PL studies important. Some of the important applications of PL are lamp phosphors and display devices. PL edge emission was extensively studied in CdS by several workers [1-3] and was related to excitonic transitions involving donor/acceptor-exciton complexes [4]. The effect of alloying of CdS, CdSe and other II-VI group compounds on the PL properties has attracted the interest of research workers in recent years. Regarding the PL spectral studies of CdS-Se, Shevel et al [5] studied the localized electronic states created by the compositional disorder in CdS-Se employing the pico-second luminescence spectral studies. Pagliara et al [6] correlated the structural disorders in CdS_xSe_{1-x} to localization of excitons observed in PL spectra. Encouraged with such results, CdS-Se was selected as the base material for the present studies. Impurities, particularly the rare earth ions play a great role in these phenomena. These ions when incorporated into a solid show distinct spectral lines of absorption and emission as a result of the electronic transitions within the $4f^N$ shell configuration [7]. The rare-earth ions are characterized by a partially filled 4f shell that is well shielded by $5s^2$ and $5p^6$ orbitals. The emission transitions, therefore, yield sharp lines in the optical spectra. The use of rare-earth element-based phosphors, therefore, based on “line-type” f-f transitions, can narrow to the visible, resulting in both light efficiency and a high lumen equivalent [8]. Bhushan and

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*Corresponding author: rss.bhilai@gmail.com coworkers [9-12] found enhancement in PL due to doping of lanthanides in (Cd-Zn)S and (Cd-Pb)S. For the present work Sm and Dy were selected as impurities. The reason for selecting Sm has been the energy levels of its emitting state $^4G_{5/2}$ lying below the energy level of the trap states in Cd(S-Se) base, hence energy transfer from host defects to rare earth activator Sm^{3+} could occur [13] and hence presented interesting activator. Dy can be expected to sensitize PL due to its well separated energy levels. Inorganic compounds using Dy as impurity have got important applications in luminescent devices like luminescent lamps, cathode ray tubes and lasers [14]. The present paper reports results of SEM, XRD, optical absorption and PL emission spectra studies of Sm and Dy doped CdS-Se (chemically deposited) films.

2. Experimental details

The films were prepared by dipping microscopic glass slides of dimension 24 x 75 mm in a mixture of 1 M solution of cadmium acetate, appropriate ratio of thiourea and sodium seleno-sulphate (prepared by heating sodium sulphite with selenium at 90^0 C for 5 hrs.), tri-ethanolamine, 0.01 M solutions of cadmium chloride, samarium nitrate/dysprosium nitrate in appropriate proportions in presence of 30% aqueous ammonia. All the chemicals used were of AR grade (make : S.D.Fine-chem. Ltd., Mumbai). Solutions of all chemicals were prepared in double distilled water. The pH value of the mixture was ~ 11. For preparing doped films, calculated proportions of 0.01M solutions of samarium nitrate and cadmium chloride were added to the original mixture. After deposition the films were cleaned by flushing with distilled water to wash out the uneven overgrowth of grains at the surface and dried in open atmosphere at room temperature (RT). The thickness of the films was measured by multiple beam interference method and was found to lie in the range 0.4694 ~ 0.4837 μm.

The PL cell consisted of films deposited on the substrates. The PL excitation source was a high pressure Hg source from which 365 nm radiation was selected by using Carl-Zeiss interference filter. An RCA-6217 photomultiplier tube operated by a highly regulated power supply was used for detection of PL light emission. The integrated light output in the form of current was recorded by a sensitive polyflex galvanometer (10^{-9} A/mm). A prism monochromator was used for PL emission spectral studies. The absorption spectra were recorded with the help of Shimadzu Pharmaspec-1700 spectrophotometer. XRD and SEM studies were performed at IUC-DAE, Indore using models Rigaku RU:H2R horizontal Rotaflex and JEOL-JSM 5600 respectively.

3. Results and discussion

SEM Studies

The SEM micrographs of different Sm and Dy doped CdS-Se films are shown in fig.-1(a), (b) (c) and (d) respectively. These configurations correspond to maximum PL and PC response respectively. Ball and leafy type structures are observed, which may appear due to layered growth of the films. This kind of structure probably appears due to layered type growth of the material, which under continued deposition forms such structure due to turning followed by overlap of different layers.

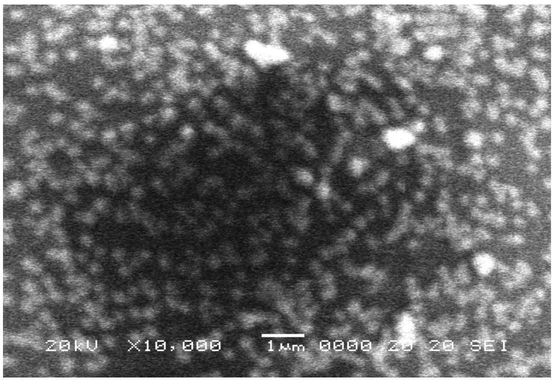

Fig.-1(a) SEM micrograph of Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Sm(3 ml) film

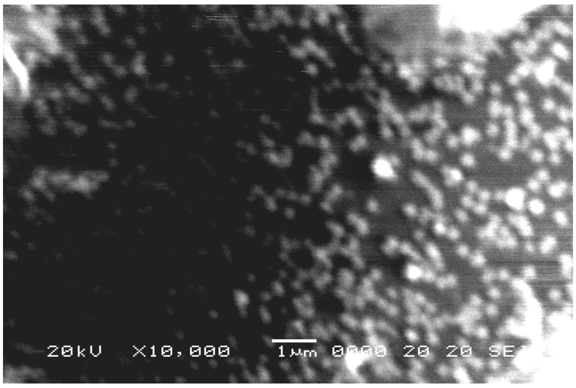

Fig.-1(b) SEM micrograph of Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Sm(3 ml) film

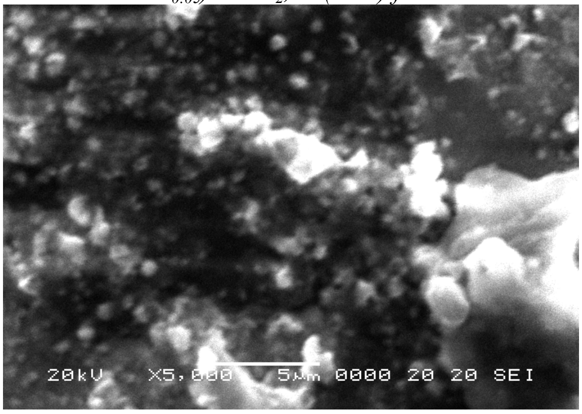

Fig.-1(c) SEM micrograph of Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Dy(6 ml) film

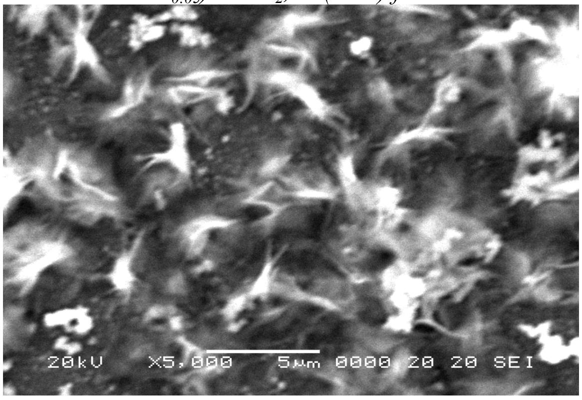

Fig.-1(d) SEM micrograph of Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Dy(2 ml) film

XRD Studies

Figs.-2(a), (b) (c) and (d) show the X-ray diffractograms of different Sm and Dy doped CdS-Se film. The assignment of peaks has been made by using JCPDS data and comparing the evaluated values of lattice constants with those of the reported values. Prominent peaks of CdS and CdSe are observed in the X-ray diffractograms. Some peaks of $CdCl_2$ and Sm are also observed. However, no peak of Dy has been observed.

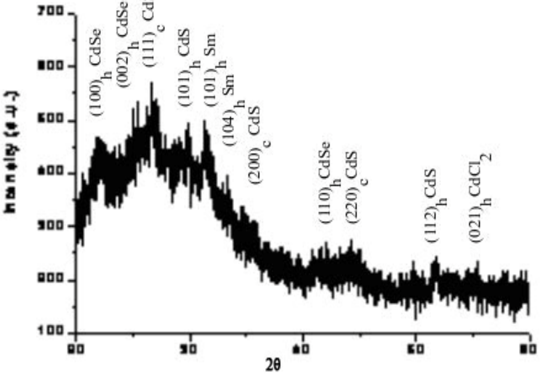

Fig.-2(a) X-ray diffractogram of Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Sm(3 ml) film

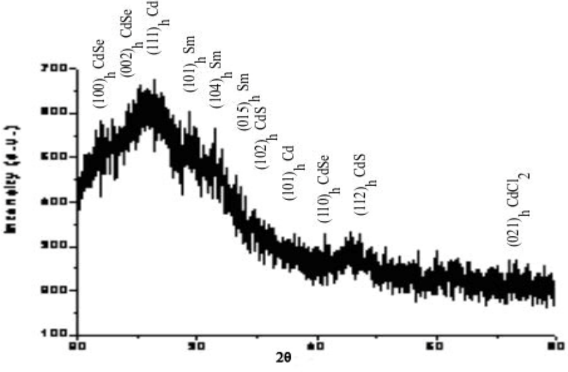

Fig.-2(b) X-ray diffractogram of Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Sm(2 ml) film

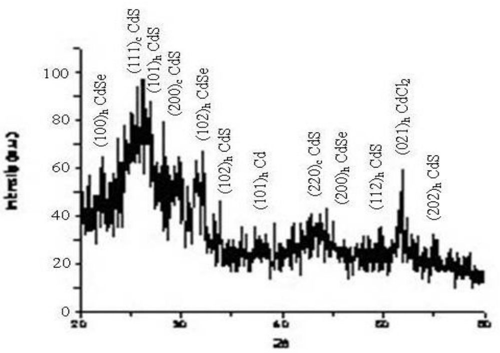

Fig.-2(c) X-ray diffractogram of Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Dy(6 ml) film

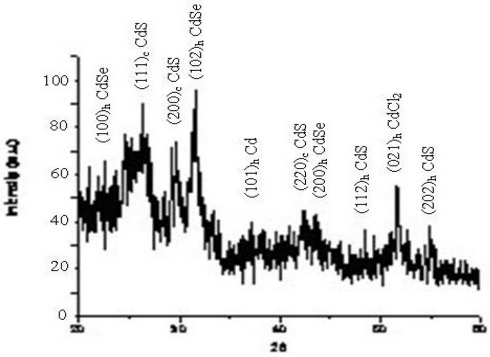

Fig.-2(d) X-ray diffractogram of Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Dy(2 ml) film

Different layers of CdS are observed in cubic as well as hexagonal phases. Such layers are known to be created through different arrangements of atomic layers. The hexagonal and cubic phases consist of sequence of atomic layers defined as ABABAB--- and that of cubic as ABCABCABC— [15]. It is also possible to find mixed forms with

Table 1 XRD data of different Cd(S-Se):$CdCl_2$,Sm/Dy films chemically deposited on glass substrate at 60^0C in WB

d-values		**Relative Intensities**		**hkl**	**Lattice-constants (^{0}A)**	
					Obs.	Rep.
Obs.	Rep.	Obs.	Rep.			
(a) **Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Sm (3ml)**						
3.7245	3.7239	91.3	100	(100)$_h$ CdSe	a=4.3	a=4.3, c=7.02
3.5010	3.51	93.2	65.85	(002)$_h$ CdSe	a= 4.3, c=7.002	a=4.3, c=7.02
3.3609	3.36	100	100	(111)$_c$ CdS	a=5.786	a=5.818
3.181	3.16	86.2	100	(101)$_h$ CdS	a=4.102, c=6.5633	a=4.135, c=6.71
3.0919	3.09	86.9	30	(101)$_h$ Sm		
2.8173	2.81	82.5	40	(104)$_h$ Sm		
2.9015	2.9	69.05	40	(200)$_c$ CdS	a=5.803	a=5.818
2.1542	2.15	45.5	82.43	(110)$_h$ CdSe	a=4.3084	a=4.3, c=7.02
2.0404	2.06	47.7	57	(220)$_c$ CdS	a=5.776	a=5.818
1.7616	1.76	42.5	45	(112)$_h$ CdS	a=4.13, c=6.758	a=4.135, c=6.71
1.658	1.658	40.73	12	(021)$_h$ $CdCl_2$	a=3.851, c=17.98	a=3.84, c=17.49
(b) **Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Sm (2ml)**						
3.7227	3.7239	91.74	100	(100)$_h$ CdSe	a=4.2986	a=4.3, c=7.02
3.5224	3.52	98.08	65.85	(002)$_h$ CdSe	a=4.2986,c=7.0448	a=4.3, c=7.02
3.3685	3.36	100	100	(111)$_c$ CdS	a=5.834	a=5.818
3.0999	3.09	88.79	30	(101)$_h$ Sm		
2.8283	2.81	83.33	40	(104)$_h$ Sm		
2.6905	2.68	76.69	40	(015)$_h$ Sm		

2.4601	2.4502	56.49	25	$(102)_h$ CdS	a=4.146, c=6.723	a=4.135, c=6.71
2.3194	2.345	47.19	100	$(101)_h$ Cd	a=2.989, c=5.569	a=2.974, c=5.62
2.1705	2.15	44.54	82.43	$(110)_h$ CdSe	a=4.304, c=7.045	a=4.3, c=7.02
1.7757	1.76	39.08	45	$(112)_h$ CdS	a=4.118, c=6.78	a=4.135, c=6.71
1.659	1.658	38.05	12	$(021)_h$ $CdCl_2$	a=3.853, c=17.90	a=3.84, c=17.49
(c) **Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Dy (6ml)**						
3.7294	3.7239	63	100	$(100)_h$ CdSe	a=4.3063	a=4.3, c=7.02
3.3615	3.36	100	100	$(111)_c$ CdS	a=5.8223	a=5.818
3.181	3.16	89.23	100	$(101)_h$ CdS	a=4.102, c=6.5633	a=4.135, c=6.71
2.914	2.9	76.07	40	$(200)_c$ CdS	a=5.828	a=5.818
2.5539	2.5542	65.23	40.59	$(102)_h$ CdSe	a=4.3063,c=7.01	a=4.3, c=7.02
2.456	2.4502	44.72	25	$(102)_h$ CdS	a=4.139, c=6.719	a=4.135, c=6.71
2.317	2.345	36.2	100	$(101)_h$ Cd	a=2.984, c=5.622	a=2.974, c=5.62
2.0589	2.058	38.46	80	$(220)_c$ CdS	a=5.8234	a=5.818
1.8639	1.862	36.69	12.72	$(200)_h$ CdSe	a=4.3045	a=4.3, c=7.02
1.7757	1.76	35.08	45	$(112)_h$ CdS	a=4.118, c=6.78	a=4.135, c=6.71
1.661	1.658	60.4	12	$(021)_h$ $CdCl_2$	a=3.851, c=17.91	a=3.84, c=17.49
1.58	1.58	24.69	7	$(202)_h$ CdS		a=4.135, c=6.71
(d) **Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Dy (2ml)**						
3.7216	3.7239	74.02	100	$(100)_h$ CdSe	a=4.2973	a=4.3, c=7.02
3.3669	3.36	90.87	100	$(111)_c$ CdS	a=5.8316	a=5.818
2.925	2.9	70.87	40	$(200)_c$ CdS	a=5.85	a=5.818
2.5551	2.5542	100	40.59	$(102)_h$ CdSe	a=4.3063,c=7.0223	a=4.3, c=7.02
2.315	2.345	38.21	100	$(101)_h$ Cd	a=2.945, c=5.573	a=2.974, c=5.62
2.0578	2.058	44.22	80	$(220)_c$ CdS	a=5.8203	a=5.818
1.8619	1.862	42.64	12.72	$(200)_h$ CdSe	a=4.2999	a=4.3, c=7.02
1.766	1.76	32.50	45	$(112)_h$ CdS	a=4.126, c=6.75	a=4.135, c=6.71
1.660	1.658	34.82	12	$(021)_h$ $CdCl_2$	a=3.849, c=17.81	a=3.84, c=17.49
1.5812	1.58	35.88	7	$(202)_h$ CdS		a=4.135, c=6.71

random stacking of very long period repeats as is found in polytypes of SiC [16]. The total crystal consists of different atomic layers of CdSe in hexagonal phases. According to Langer et al [17], one might think of solid solutions as mixtures of microcrystalline regions of pure CdSe and CdS, where each microregion might consist of a number of unit cells of each material. Such a model can explain uniform shift of absorption edge with variation in composition. A possibility of solid solution consisting of statistical distribution of CdSe and CdS with respect to their overall concentration was also mentioned by these workers.

Optical absorption studies

Optical absorption spectra of different CdS-Se films are shown in figs.-3(a) and (b). The films prepared with different mole % of S and Se show variation in the band gap over different compositional range (e.g. $CdS_{0.95}Se_{0.05}$: 2.36 eV, $CdS_{0.7}Se_{0.3}$: 2.19 eV) indicating the formation of a common lattice of CdS-Se through solid solutions. A steep increase in the absorption corresponding to the onset of band-to band transition is observed in the curves. Further, the optical absorbance decreases in presence of impurity as is shown for Sm and Dy doped films in curves 3(a) and (b) respectively. The curves of doped films are flat and extended in impurity doped films showing incorporation of more energy levels in the band gap due to impurities. With increasing concentration of Se, magnitude and width of absorption decrease. A narrow and resolved absorption peak corresponds to narrower size distribution. It is known that in nano-crystalline materials the energy spectrum is quantized and the highest occupied valence band and lowest unoccupied conduction band are shifted to more positive and negative values resulting in a blue shift in absorption edge onset of direct absorption.

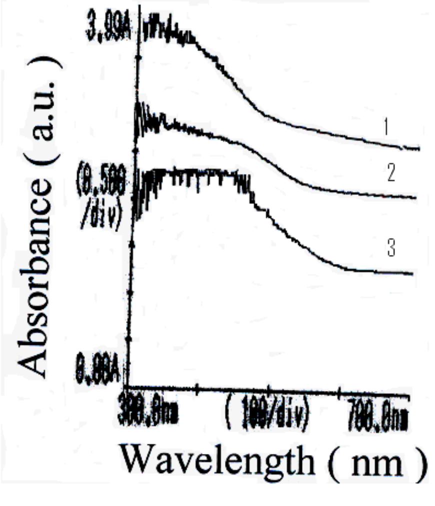	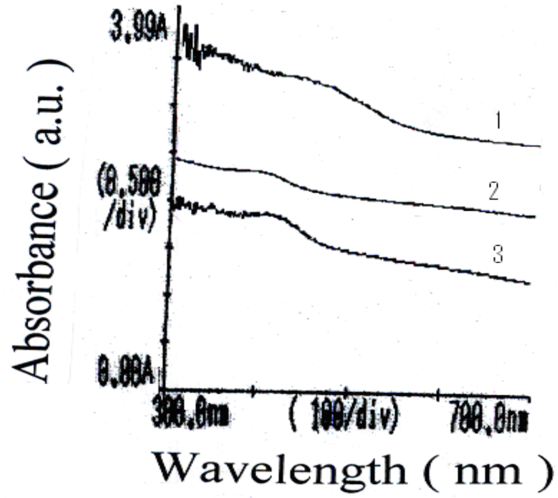
Fig.-3(a) Optical absorption spectra of: *1. Cd($S_{0.95}$-$Se_{0.05}$), 2. Cd($S_{0.95}$-$Se_{0.05}$):CdCl$_2$,Sm (3 ml) and 3. Cd($S_{0.95}$-$Se_{0.05}$):CdCl$_2$,Dy (6 ml).*	*Fig.-3(b) Optical absorption spectrum of :* *1. Cd($S_{0.7}$-$Se_{0.3}$), 2. Cd($S_{0.7}$-$Se_{0.3}$):CdCl$_2$,Sm (2 ml) and 3. Cd($S_{0.7}$-$Se_{0.3}$):CdCl$_2$,Dy (2 ml).*

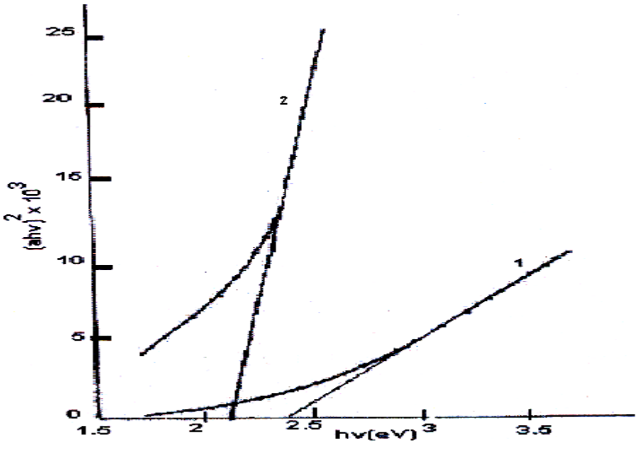

Fig.-4 Tauc's plot of Cd(S-Se) films : 1. Cd($S_{0.95}$-$Se_{0.05}$), 2. Cd($S_{0.7}$-$Se_{0.3}$).

The optical absorption of Sm doped film a weak hump at around 404 nm [curve 2, fig.3(b)] corresponds to the direct excitation from ground $^6H_{5/2}$ to higher energy levels dominant excitation to $^4K_{11/2}$ states of Sm^{3+} ion. Similarly in Dy doped films a hump is observed at around 464 nm [curve 3, fig.3(b)]. Yu Chun Li et al [18] have shown that, after excitation with wavelengths 458 nm and 478 nm corresponding to the direct excitation from ground $^6H_{15/2}$ to higher energy levels dominant excitation to $^4I_{19/2}$ and $^4F_{9/2}$ states of Dy^{3+} ion.

PL Emission spectra

Fig.-5 shows PL emission spectra of CdS and CdS-Se films at different compositions of S and Se. The emission spectrum of CdS shows a single peak at 515 nm

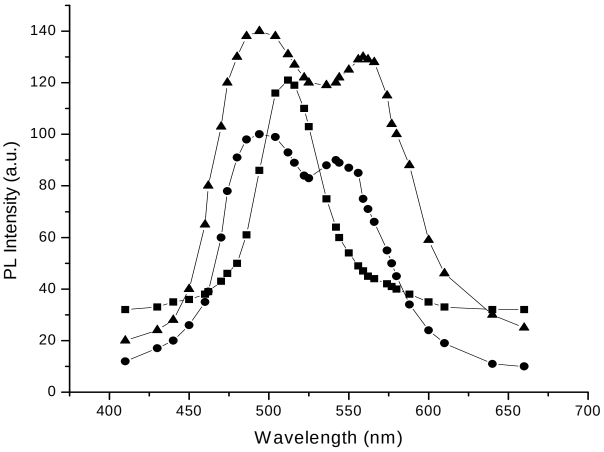

Fig.-5 PL emission spectra of different Cd(S_{1-x}-Se_x) films prepared at 60^0C with different values of x: ■ CdS, ♦ Cd($S_{0.95}$-$Se_{0.05}$) and ▲Cd($S_{0.7}$-$Se_{0.3}$).

and those of CdS-Se films show two peaks. The emission peak at 511 nm of CdS corresponds to band gap 2.42 eV and so it can be assumed to be the edge emission of CdS. Thomas and Hopfield [19] attributed the edge emission to transitions associated with donor/acceptor exciton complexes. Jeong and Yu [20] observed the excitonic effects in CdS at RT. Thus, in present cases also the edge emission can be attributed to excitonic transitions. The PL emission in CdS-Se is significantly broader than pure CdS and CdSe due to excitonic effects [21]. In the present studies, two broad peaks are observed in CdS-Se. The peak observed at ~516 nm shows a shift towards higher wavelengths upto 577 nm with increasing mole % of Se corresponding to reduction in band gap. So, this emission can be identified as edge emission of CdS-Se. Due to similar excitonic nature of emissions in both CdS and CdSe this emission can be attributed to radiative decay of free exciton. The position of broad band at 494 nm remains unchanged and may be attributed to excitons bound to neutral donor levels formed by suphur/excess Cd. In present method, excess Cd was produced as was confirmed by EDX studies whereas sulphur was produced in solid phase by thiourea and sodium thiosulphate both which can be substituted in the lattice. For increasing concentration of Se, higher volumes of sodium selenosulphate were added resulting in formation of more sulphur thus enhancing the emission in its presence.

The PL emission spectra of Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Sm (2ml) and Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Dy (2ml) films are shown in fig.-6.

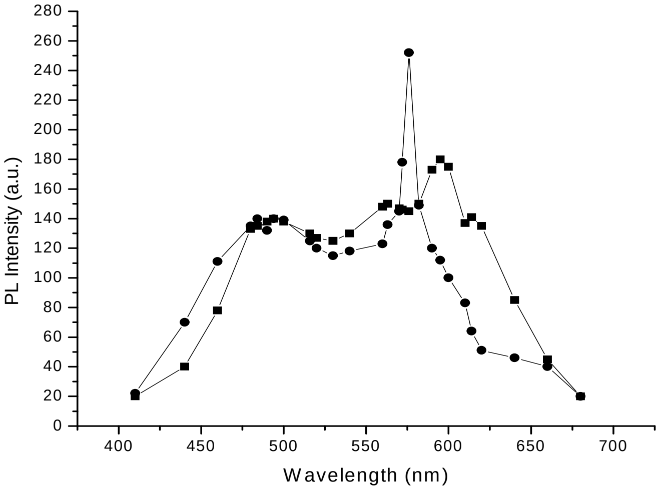

Fig.-6 PL emission spectra of ■ *Cd(S*$_{0.7}$*-Se*$_{0.3}$*):CdCl*$_2$*,Sm (2 ml) and* ● *Cd(S*$_{0.7}$*-Se*$_{0.3}$*):CdCl*$_2$*,Dy (2 ml) films.*

In Sm doped films, the PL emissions correspond to transitions $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ giving emissions at 563, 595 and 614 nm. Similarly, in Dy doped films, the PL emissions observed at 495 nm and 545 nm are related to transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$. These transitions have been shown in fig.-7(a) and (b) respectively.

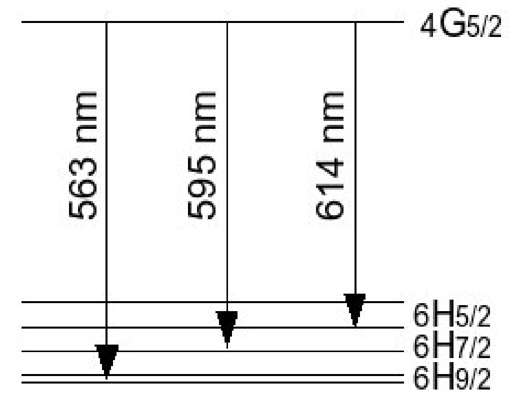	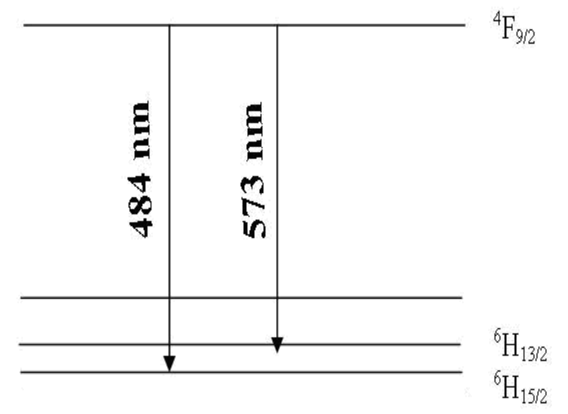
Fig.-7(a) Schematic diagram showing various emission transitions in Cd(S$_{0.7}$*-Se*$_{0.3}$*):CdCl*$_2$*,Sm(2ml) films.*	*Fig.-7(b) Schematic diagram showing various emission transitions in Cd(S*$_{0.7}$*-Se*$_{0.3}$*):CdCl*$_2$*,Dy (2ml) films.*

4. Conclusions

The chemically deposited CdS-Se films show layered growth morphology in the SEM studies. In XRD studies, existence of CdS, CdSe, $CdCl_2$ and Sm are found. PL emission spectra of the CdS-Se films show two peaks in absence of impurities. Presence of impurities is found in terms of transitions in these elements. Absorption studies also support their existence.

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References

[1] R.E.Halsted, M.Aven, Phys. Rev. Lett. **14**, Y533(2-1)-Y533 (2-2) (1965).

[2] S.Iida and M.Toyama, J. Phys. Soc. (Japan) **31**, 190-194 (1971).

[3] Y.Kokubun and T.Kaeriyama, J. Appl. Phys. (Japan) **14**, 1403-1404 (1975).

[4] D.G. Thomas and J.J. Hopfield, Phys. Rev. **128**, 2135-2148 (1962).

[5] S. Shevel, R. Fischer, G. Noll, E.O. Gobel, P. Thomas and C. Klingshirn, J. Lum. **37**, 45-50 (1987).

[6] S. Pagliara, L. Sangaletti, L.E. Depero, V. Capozzi and G. Perna, Appl. Surf. Sci. **186**, 527-532 (2002).

[7] P. Gupta, S. Choudhary and A.K. Pal, J. Phys. D. Appl. Phys. **26**, 1709-1713 (1993).

[8] N. Yukami, M. Ikeda, Y. Harada, M. Nishikura and T. Nishikura, Electronic Devices (IEEE) **33**, 520-525 (1986).

[9] S. Bhushan, M. Mukherjee and P. Bose, Rad. Effect and Defects in Solids **153**, 367-377 (2001).

[10] M. Mukherjee and S. Bhushan, Opt. Mater. **22**, 51-56 (2003).

[11] T. Chandra and S. Bhushan, J. Mater. Sci. **39**, 6303-6309 (2004).

[12] S. Bhushan and S. Shrivastava, Opt. Mater. **28**, 1334-1340 (2006).

[13] K.L. Frindel, M.H. Bartl, M.R. Robinson, G.C. Bazan, A. Popitsch and G.D. Stucky, J. Solid State Chem. **172**, 81 (2003).

[14] P. Dorenbos, J. Lum. **91**, 91-106 (2000).

[15] C. Kittel, Introduction to Solid State Physics (7th edition) (John Wiley & Sons) p.18, (1995).

[16] Ibach Herald and Lüth Hans, Solid State Physics (An Introduction to Theory and Expt.) (Springer International Student Edn.) p.25 (1991).

[17] D.W. Langer, Y.S. Park and R.N. Euwama, Phys. Rev. **152**, 788 (1966).

[18] Li Yu-Chun, Chang Yen-Hwei, Lin Yu-Feng, Chang Yee-Shin & Lin Yi-Jing, J. Alloys and Compounds **439**, 367 (2007).

[19] D.G. Thomas and J.J. Hopfield, Phys. Rev. **128**, 2135-2148 (1962).

[20] T.S. Jeong and P.Y. Yu, J. Phys. Soc. (Korea) **36**, 102-105 (2000).

[21] S. Shevel, R. Fischer. G. Noll, E.O. Gobel, P. Thomas and C. Klingshirn, J. Lum. **37**, 45-50 (1987).