JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 11, November 2010, p. 2221 - 2225

Structural and optical studies on Pr^{3+} doped chemically deposited Cd(Se-S) films

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Results of SEM and XRD studies, optical absorption spectra and photoluminescence (PL) emission studies are reported for Cd(Se-S):$CdCl_2$,Pr 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 CdSe and CdS along with lines of $CdCl_2$. The chemically deposited CdSe-S 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 excess sulphur/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 Pr doped films, a new intense peak appears at 598 nm (as compared to the PL spectra of base material), which may be related to the transitions in Pr-levels.

(Received October 18, 2010; accepted November 19, 2010)

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

1. Introduction

II–VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS, CdSe, CdTe, etc), are considered to be very important materials for a wide spectrum of opto-electronic applications as having specific physical properties such as direct bandgap width and sensitive to infrared part of solar spectrum, good electrical properties and increased capability in obtaining adjustable n- or p-type conductivity by doping. Particularly, in the visible and near infrared, direct bandgaps of CdSe (1·75 eV) and CdS (2·44 eV), respectively make them candidates for the conversion of low energy light into electricity. Moreover, homogeneous alloys formed over the entire composition range by combination of these compounds allow the production of very interesting ternary $Cd(Se_x - S_{1-x})$ $(0{\cdot}1 < x < 1)$ system [1]. Some of the important applications of PL of such materials lie in lamp phosphors and display devices. PL edge emission was extensively studied in CdS by several workers [2-4] and was related to excitonic transitions involving donor/acceptor-exciton complexes [5]. 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 CdSe-S, Shevel et al [6] studied the localized electronic states created by the compositional disorder in CdS-Se employing the pico-second luminescence spectral studies. Pagliara et al [7] correlated the structural disorders in $CdSe_xS_{1-x}$ to localization of excitons observed in PL spectra. Encouraged with such results, CdSe-S 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 [8]. 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 [9]. Bhushan and coworkers [10-13] found enhancement in PL due to doping of lanthanides in (Cd-Zn)S and (Cd-Pb)S. Pr can be expected to sensitize PL due to its well separated energy levels. The present paper reports results of SEM, XRD, optical absorption and PL emission spectra studies of Pr^{3+} doped CdSe-S (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 selenosulphate (prepared by heating sodium sulphite with selenium at 90^0 C for 5 hrs.), tri-ethanolamine, 0.01 M solutions of cadmium chloride, praseodymium 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 praseodymium 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 0.546 ~ 0.583 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 scanning electron microscope equipped with Oxford/Link EDS respectively.

3. Results and discussion

3.1 SEM Studies

The SEM micrographs of the Pr doped CdSe-S films are shown in fig.-1(a). Ball type structure is 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. The EDX measurement made on Cd(Se-S) powder, obtained from the precipitate, is shown in fig.-2 and corresponding elemental analysis are presented in table-1. Existence of different element of Cd, Se and S are obtained with excess of Cd.

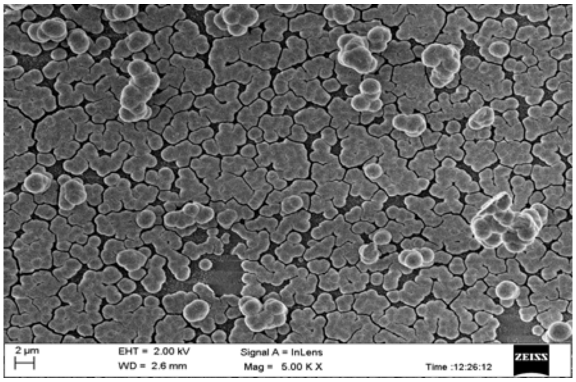

Fig.-1 SEM micrograph of chemially deposited Cd($Se_{0.95}$-$S_{0.05}$):$CdCl_2$,Pr film

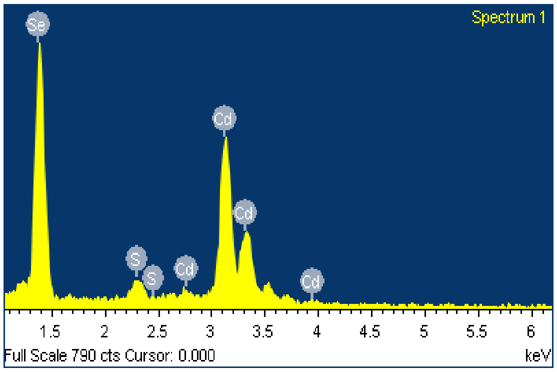

Fig.-2 EDX spectrum of chemically deposited Cd($Se_{0.95}$-$S_{0.05}$) film.

Table 1. EDX elemental analysis data of Cd(S-Se) powder.

Element	Weight%	Atomic%
S K	2.33	6.54
Se L	45.38	51.65
Cd L	52.29	41.81
Totals	100.00	

3.2 XRD Studies

Figs.-3 shows the X-ray diffractogram of the Pr doped CdSe-S 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. The corresponding data is presented in table-2. Prominent peaks of CdS and CdSe are observed in the X-ray diffractograms. One peak of $CdCl_2$ is also observed.

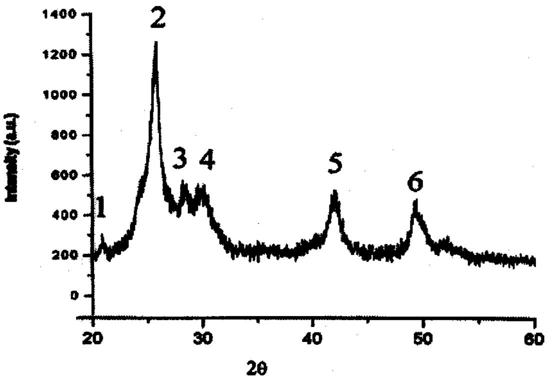

Fig. 3 X-ray diffractogram of Cd($Se_{0.95}$- $S_{0.05}$):$CdCl_2$,Pr film.

Different layers of CdS are observed in cubic as well as hexagonal phases. As explained in earlier papers, 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—[14]. It is also possible to find mixed forms with random stacking of very long period repeats as is found in polytypes of SiC [15]. The total crystal consists of different atomic layers of CdSe in hexagonal phases. According to Langer et al [16], 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.

Table 2. XRD data of Cd($Se_{0.95}$-$S_{0.05}$):$CdCl_2$,Pr film chemically deposited on glass substrate at 60^0C in WB

Peak No	d-values		Relative Intensities		hkl	Lattice-constants	
	Obs.	Rep.	Obs.	Rep.		Obs.	Rep.
1	3.724	3.7239	26	100	$(100)_h$ CdSe	a = 4.29	a=4.3, c=7.02
2	3.362	3.36	100	100	$(111)_c$ CdS	a = 5.82	a=5.818
3	2.87	2.9	44	40	(200)c CdS	a = 5.79	a=5.818
4	3.088	2.5542	42	40.59	$(102)_h$ CdSe	a = 3.621	a=4.3, c=7.02
5	2.059	2.058	40	80	$(220)_c$ CdS	a = 5.83	a=5.818
6	1.66	1.658	38	12	$(021)_h CdCl_2$	a = 3.85	a=3.84, c=17.49

3.3 Optical absorption studies

Optical absorption spectra of different CdS-Se films are shown in figs.-3(a) and (b). The optical absorbance is found to decrease in presence of impurity as is shown for Pr doped film in curves. In the optical absorption of Pr doped film a weak hump at around 451 [curve 2, fig.3(b)] corresponds to the direct excitation from ground $^2F_{5/2}$ to higher energy level dominant excitation to $^3P_2$ state of Pr^{3+} ion.

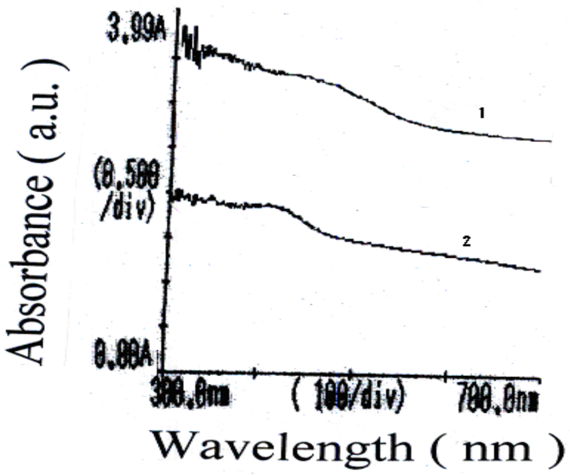

Fig. 3(b) Optical absorption spectrum of: 1. Cd($S_{0.95}$-$Se_{0.05}$) film, 2. Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Pr film.

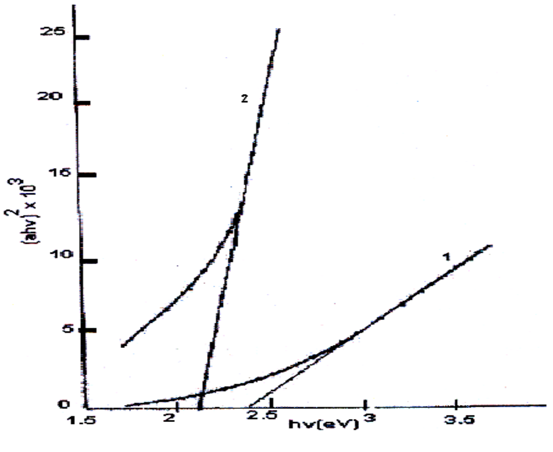

Fig. 4. Tauc's plot of: 1. Cd($S_{0.95}$-$Se_{0.05}$) film, 2. Cd($S_{0.95}$-$Se_{0.05}$):$CdCl_2$,Pr film.

3.4 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 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 [17] attributed the edge emission to transitions associated with donor/acceptor exciton complexes. Jeong and Yu [18] 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 [19]. 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.

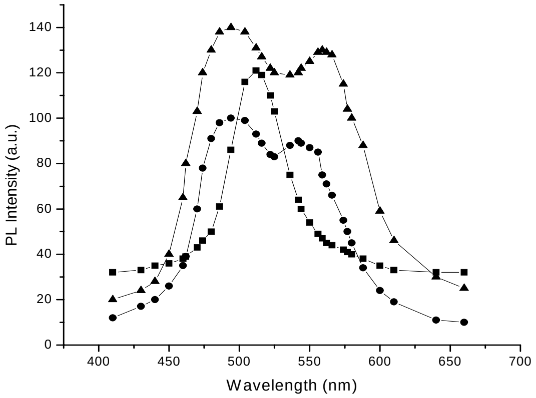

Fig.5. PL emission spectra of different Cd(S_{1-x}-Se_x) films prepared at 60^0C with different values of x: ■ CdS, ♦ Cd($Se_{0.95}$-$S_{0.05}$) and ▲ Cd($Se_{0.95}$-$S_{0.05}$):$CdCl_2$

The PL emission spectrum of Cd($Se_{0.95}$-$S_{0.05}$):$CdCl_2$,Pr film is shown in fig.-6. In the Pr doped film, the PL emissions correspond to transitions $^1D_2 \rightarrow {}^3H_4$ giving emission at 598 nm.

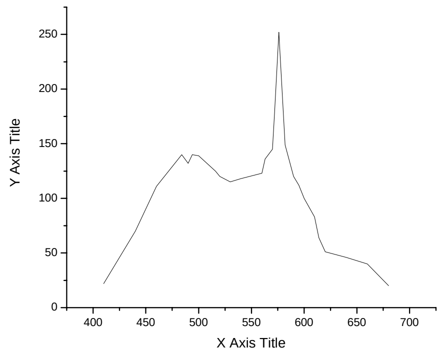

Fig.-7(a) Schematic diagram showing various emission transitions in the Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Pr film

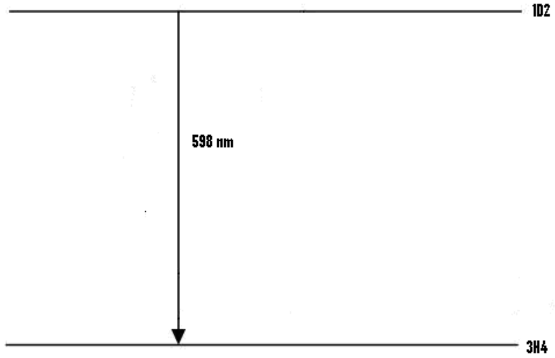

Fig. 7(b) Schematic diagram showing emission transition in the Cd($S_{0.7}$-$Se_{0.3}$):$CdCl_2$,Pr film

4. Conclusions

The chemically deposited CdS-Se films show layered growth morphology in the SEM studies. In XRD studies, existence of CdS, CdSe and $CdCl_2$ 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.

Acknowledgements

The authors are grateful to IUC-DAE, Indore (M.P.) for SEM and XRD studies and to UGC-CRO, Bhopal for providing the financial assistance through the project F.N.-MS-56/202024/09-10 to one of the authors (RSS).

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