STRUCTURAL AND OPTICAL STUDIES OF 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 different CdS_x-Se_{1-x} films prepared by chemical bath deposition method on glass substrates at 60^0C in a water bath (WB). SEM studies show ball and leafy type structures with voids which is related to layered growth. XRD studies show diffraction lines of CdS and CdSe. 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).

1. Introduction

CdS/CdSe are direct band gap semiconductors belonging to II-VI group. The structural and optical properties, as well as good chemical and mechanical stability, recommends CdS/CdSe as semiconductors well suited for opto-electrical applications, such as IR detectors or solar cells., etc. 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_x-Se_{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. CdS-Se has advantage over CdS in changing the band gap of the material [for CdS : E_g = 2.4 eV, for CdSe : E_g = 1.7 eV] which subsequently influences its electro-optical properties.

In the present paper, various characterization techniques such as SEM, XRD, optical spectroscopy are employed to study the different CdS_x-Se_{1-x} films, not explored earlier and the corresponding results are discussed.

2. Experimental details

Chemical bath deposition technique was used to deposit films of CdS-Se on glass substrates (cleaned with acetone and doubled distilled water) of dimensions (24 mm x 75 mm) dipped vertically into a mixture of solutions of 1M cadmium acetate, appropriate ratio of thiourea

and sodium seleno-sulphate [Na_2SeSO_3] solution { prepared by heating elemental selenium (99.9% pure) in aqueous solution of sodium sulphite [Na_2SO_3] at 90^0C for 5 hrs.}, triethanolamine and 30% aqueous ammonia. All the chemicals used were of AR grade (make : S.D.Fine-chem. Ltd., Mumbai). All the solutions were prepared in double distilled water. After the depositions, the films were cleaned by flushing with distilled water and then dried by keeping the samples in open atmosphere at room temperature.
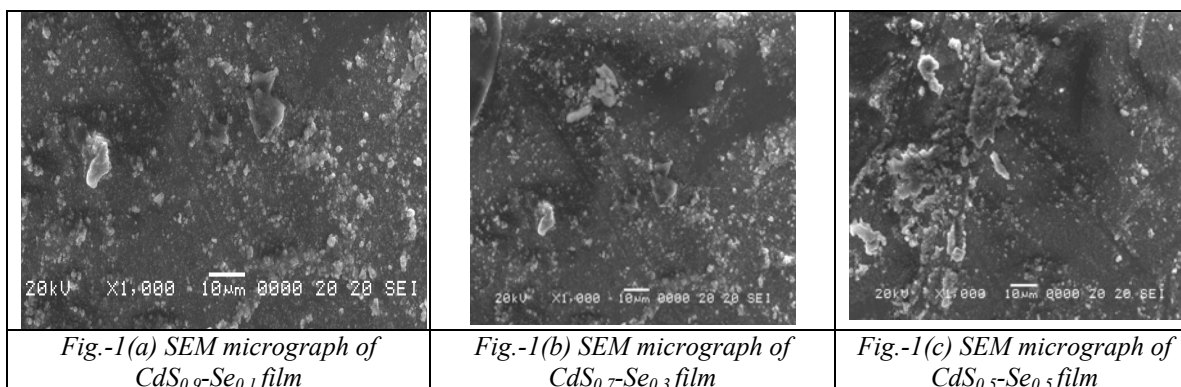
Triethanolamine and ammonia solution were used to adjust pH of the reaction mixture and to increase film adherence. To obtain good quality films time, temperature of deposition and pH of the solution were optimized. The optimum time, temperature and pH were observed to be 1 hr., 60^0C and 11.2 respectively. Film thickness were determined by optical interference method and were found to lie in the range of 0.4694 ~ 0.4837 μm.

SEM and XRD studies were performed at IUC-DAE, Indore using models Rigaku RU:H2R horizontal Rotaflex and JEOL-JSM 5600 respectively. The absorption spectra were recorded with the help of Shimadzu Pharmaspec-1700 spectrophotometer. 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.
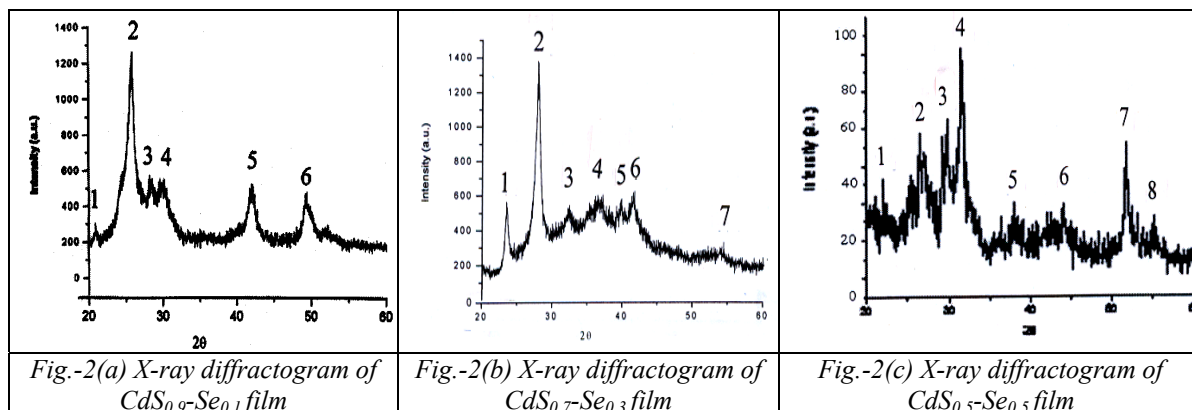
3. Results and discussions

SEM Studies

The SEM micrographs of different CdS_x-Se_{1-x} films are shown in figs.-1(a), (b) and (c) 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* $CdS_{0.9}$-$Se_{0.1}$ *film* | *Fig.-1(b) SEM micrograph of* $CdS_{0.7}$-$Se_{0.3}$ *film* | *Fig.-1(c) SEM micrograph of* $CdS_{0.5}$-$Se_{0.5}$ *film* |

XRD Studies

Figs.-2(a), (b) and (c) show the X-ray diffractograms of different CdS_x-Se_{1-x} films and the corresponding data are presented in table 1. 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.

| Fig.-2(a) X-ray diffractogram of CdS$_{0.9}$-Se$_{0.1}$ film | Fig.-2(b) X-ray diffractogram of CdS$_{0.7}$-Se$_{0.3}$ film | Fig.-2(c) X-ray diffractogram of CdS$_{0.5}$-Se$_{0.5}$ 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—[7]. It is also possible to find mixed forms with random stacking of very long period repeats as is found in polytypes of SiC [8]. The total crystal consists of different atomic layers of CdSe in hexagonal phases. According to Langer et al [9], 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 1 XRD data of different CdS$_x$-Se$_{1-x}$ films chemically deposited on glass substrate at 60^0C.

Peak No	d-values		Relative Intensities		hkl	Lattice-constants	
	Obs.	Rep.	Obs.	Rep.		Obs.	Rep.
(a)	**CdS$_{0.9}$-Se$_{0.1}$ film**						
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
(b)	**CdS$_{0.7}$-Se$_{0.3}$ film**						
1	3.724	3.7239	43	100	(100)$_h$ CdSe	a = 4.33	a=4.3, c=7.02
2	3.362	3.36	100	100	(111)$_c$ CdS	a = 5.823	a=5.818
3	2.55	2.5542	38.9	40.59	(102)$_h$ CdSe	a=4.31, c=7.01	a=4.3, c=7.02
4	2.059	2.058	41.2	80	(220)$_c$ CdS	a = 5.83	a=5.818
5	2.32	2.345	42.3	100	(101)$_h$ Cd	a=2.9983, c=5.623	a=2.974, c=5.62
6	2.11	2.15	44.5	82.43	(110)$_h$ CdSe	a = 4.29	a=4.3, c=7.02
7	1.66	1.658	21	12	(021)$_h$CdCl$_2$	a = 3.85	a=3.84, c=17.49
(c)	**CdS$_{0.5}$-Se$_{0.5}$ film**						
1	3.7245	3.7239	91.3	100	(100)$_h$ CdSe	a=4.3	a=4.3, c=7.02
2	3.3609	3.36	100	100	(111)$_c$ CdS	a=5.786	a=5.818
3	3.181	3.16	86.2	100	(101)$_h$ CdS	a=4.102, c=6.5633	a=4.135, c=6.71

4	3.0919	3.09	86.9	30	(101)$_h$ Sm	a = 3.64	a = 3.629, c=26.2
5	2.1542	2.15	45.5	82.43	(110)$_h$ CdSe	a=4.3084	a=4.3, c=7.02
6	2.0404	2.06	47.7	57	(220)$_c$ CdS	a=5.776	a=5.818
7	1.7616	1.76	42.5	45	(112)$_h$ CdS	a=4.13, c=6.758	a=4.135, c=6.71
8	1.658	1.658	40.7 3	12	(021)$_h$ CdCl$_2$	a=3.851	a=3.84, c=17.49

Optical Absorption Studies

The optical absorption measurements of the Sm doped CdS$_x$-Se$_{1-x}$ films have been carried out at room temperature by placing an uncoated identical glass substrate in the reference beam. The optical spectra of the films have been recorded in the wavelength range 300-700 nm. The energy band gaps of these films were determined from absorption spectra. Almost all the II-VI compounds are direct band gap semiconductors. According to Tauc's relation, the absorption coefficient for direct band gap materials is given by [10]:

$$\alpha h\nu = A (h\nu - E_g)^{\frac{1}{2}} \qquad (4)$$

where $\alpha h\nu$ is the photon energy, E_g is the band gap and A is a constant (called absorbance) which is different for different materials. The absorption coefficient α may be written in terms of absorbance A as [11]:

$$\alpha = 2.303 \ A \ / \ t \qquad (5)$$

where t = thickness of the film.

Optical absorption spectra of different CdS$_x$-Se$_{1-x}$ films are shown in fig.-3 [with absorbance (A) {arb. units} on ordinate and wavelength.(λ){nm}on abscissa]. The films prepared with different mole % of S and Se show variation in the band gap over different compositional range (e.g. CdS$_{0.9}$-Se$_{0.1}$: 2.36 eV, CdS$_{0.7}$-Se$_{0.3}$: 2.19 eV and CdS$_{0.5}$-Se$_{0.5}$: 2.1 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. 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.
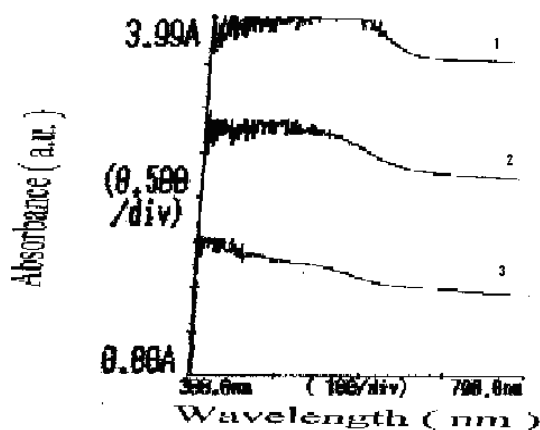

Fig.3. Optical absorption spectra of : (1) CdS$_{0.9}$-Se$_{0.1}$film, (2) CdS$_{0.7}$-Se$_{0.3}$film and (3) CdS$_{0.5}$-Se$_{0.5}$film

When a graph is plotted between $(\alpha h\nu)^2$ on ordinate, vs $h\nu$ on abscissa, a behaviour shown in fig.- 4 is obtained. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap of the film material for the Cd(S-Se):CdCl$_2$,Sm film .
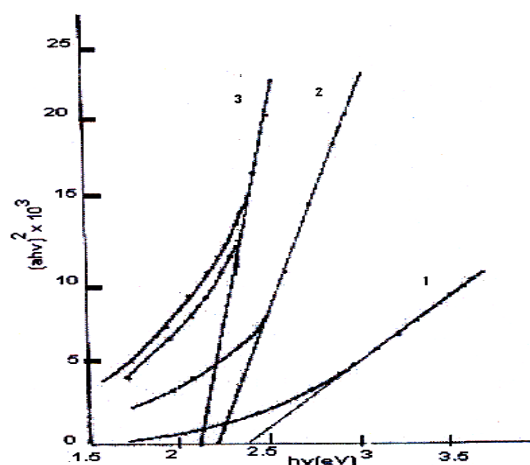

Fig. 4. Tauc's plot of Cd(S-Se) films : 1. CdS$_{0.95}$-Se$_{0.05}$, 2. CdS$_{0.7}$-Se$_{0.3}$ and 3. CdS$_{0.5}$-Se$_{0.5}$.

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 [12] attributed the edge emission to transitions associated with donor/acceptor exciton complexes. Jeong and Yu [13] 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 [14]. 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.

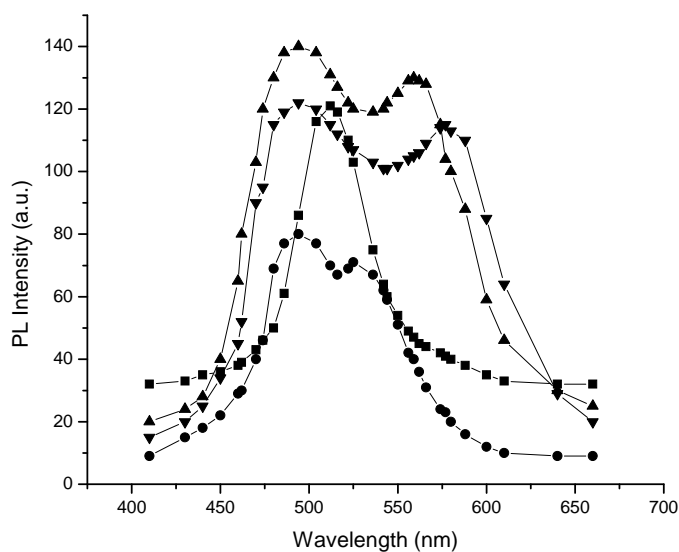The PL emission spectra of different CdS$_x$-Se$_{1-x}$ films are shown in fig.-5.

Fig. 5. PL emission spectra of different $Cd(S_{1-x}-Se_x)$ films prepared at 60^0C with different values of x: ■ CdS, ♦ $CdS_{0.9}-Se_{0.1}$, $CdS_{0.7}-Se_{0.3}$ and $CdS_{0.5}-Se_{0.5}$.

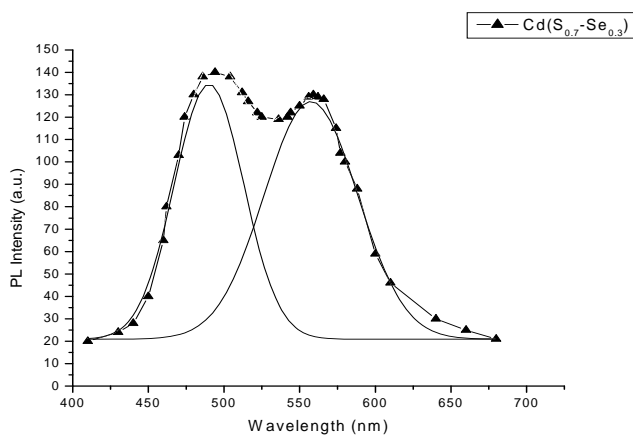*Fig.6. Original peak of PL emission spectrum of Cd(S0.7-Se0.3) is deconvoluted into two Lorentzian curves located at 494 nm and 559 nm.*

PL emission spectra of $Cd(S_{0.7}-Se_{0.3})$ films consist of two peaks that can be deconvoluted into into two Lorentzian curves one at 494 nm and the other at 559 nm [fig.-6]. These peaks have been attributed to the radiative decay of free exciton and exciton-donor complexes found in presence of S / excess Cd, respectively.

4. Conclusions

The chemically deposited CdS_x-Se_{1-x} films show layered growth morphology in the SEM studies. In XRD studies, existence of CdS and CdSe are found. Optical absorption spectra show good absorption with spikes near 300 nm. PL emission spectra of the CdS-Se films show two peaks.

Acknowledgements

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