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EXCITONIC PHOTOLUMINESCENCE EMISSION OF CHEMICALLY DEPOSITED CdS_xSe_{x-1} FILMS

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In the present work, a study on the optical absorption and emission of CdS_xSe_{x-1} thin films is reported. The CdS_xSe_{x-1} films deposited by chemical bath deposition method show excitonic transitions in optical absorption and photoluminescence (PL) spectral studies at room temperature. The PL emission peaks are related to Ex (A) free exciton and their LO- phonon replica. The effect of impurities like excess cadmium and excess sulfur on the PL emission peaks is also analyzed.

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1. Introduction

The ternary compound CdS_xSe_{x-1} is a highly photosensitive material, so it has many practical applications in devices like photo resistors, optical filters, signal memory devices, laser screens, LSI circuits, Infrared imaging devices, Optoelectronic switches, Electro photography, Image intensifiers and exposure meters [1-5]. The knowledge of the optical properties of these films is very important for study of optoelectronic devices, particularly solar cells. In the present work, we report a study on the optical properties such as optical absorption and emission of CdS_xSe_{x-1} thin films prepared by a cost effective and simple chemical bath deposition. The films were characterized by x-ray diffraction and scanning electron microscopy.

A remarkable change in the morphology, structure, and optical absorption as well as PL emission spectra is observed with the change in the ratio of cations and anions. Such studies give an insight into the fundamental processes which affect the physical properties of the functional materials like CdS-Se . Moreover, The absorption edge emission of CdS and CdSe are excitonic in nature. The excitonic transitions are observed even at room temperature in ternary II-VI compounds like CdS_xSe_{x-1} due to potential fluctuations. These transitions produce lasing in CdS type materials, so their study is important in development of thin film solid state lasers.

2. Experimental

Films were prepared by taking 1M solutions of cadmium acetate, thio urea, triethanolamine (TEA), 30% aqueous ammonia and .01M solutions of $CdCl_2$ prepared in double distilled water. TEA and aqueous ammonia work as complexing agents, which slow down the rate of release of CdS-Se and we get a layer by layer deposition of smooth, pinhole free and well adherent films. The source of selenide ions was a freshly prepared solution of sodium seleno sulphate, the method of preparation has been reported elsewhere [6]. For preparing films with excess sulfur $Na_2S_2O_3$ was used instead of Na_2SO_3. $Na_2S_2O_3$ introduces colloidal sulfur which can be easily incorporated into the lattice [6]. These solutions were mixed in appropriate proportions. The pH value of such mixture was kept ~ 10. Films were prepared on glass substrate, in water bath at 60^oC. The deposition was based on precipitation followed by condensation in

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static conditions. After deposition the films were cleaned with distilled water and dried in open atmosphere at room temperature. It was observed that the films prepared without excess sulfur were rough and bright orange in colour whereas those prepared with excess sulfur were smoother and yellowish. Out of various films prepared, films with equal thicknesses were used for absorption and emission studies so that their results could be compared.

The PL and optical absorption studies were done at the optoelectronics laboratory of S. O. S. in physics, Pt. Ravishankar Shukla University, Raipur (C.G.). For the PL studies a high pressure mercury excitation source was used with a Carl Zeiss filter to select 365nm radiation. The detection of emission was done using a RCA-6217 photomultiplier tube and a grating monochromator. For the study of optical absorption and transmittance spectra Shimadzu (UV-VIS) Pharmaspec-1700 spectrophotometer was used. 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

The SEM micrographs and X-ray diffractograms of the films prepared with and without excess sulfur are shown in Fig. (1–4).

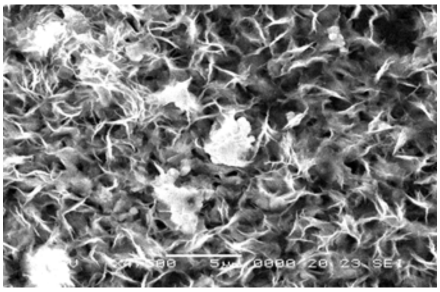

Fig. 1. SEM micrograph of $CdS_{0.95}Se_{0.05}$ film at a magnification of 4500X , prepared without excess sulfur

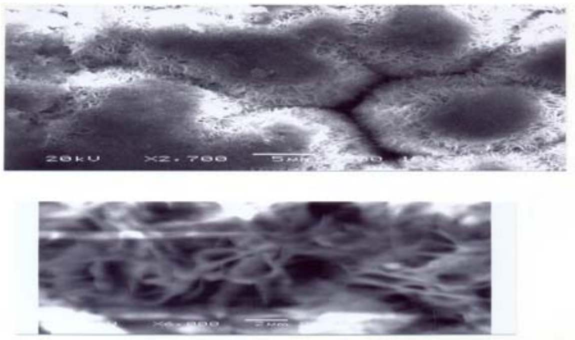

Fig. 2. SEM micrograph of $CdS_{0.95}Se_{0.05}$ film at a magnification of 6000X , prepared with excess sulfur.

On comparing the SEM micrographs (Fig. 1 & 2) we observe that films prepared without excess sulfur show grains spread over a fibrous background, whereas in the films prepared with excess sulfur only fibrous structures are observed and the grains are missing. So the morphologies of the films are quite different. In fact as we increase the percentage of selenium the fibrous structure of the films prepared with excess sulfur becomes more prominent and the films prepared without excess sulfur show a crystalline nature (the SEMs shown in previous publication [6]). These fibrous chain-like structures are characteristics of sulfur or selenium present in the samples.

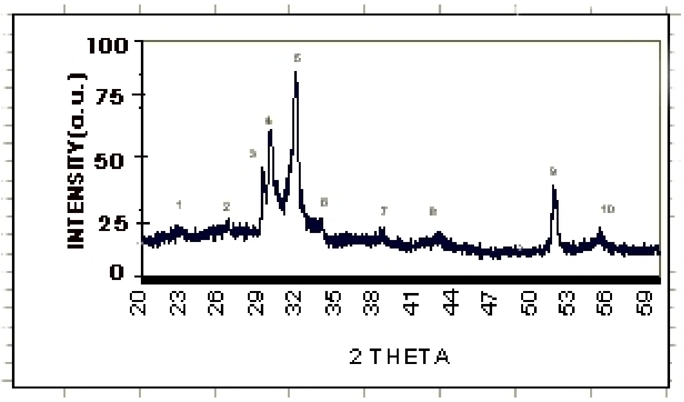

Fig. 3. X-ray Diffractogram of CdS$_{0.95}$Se$_{0\cdot 05}$ film without excess sulfur.

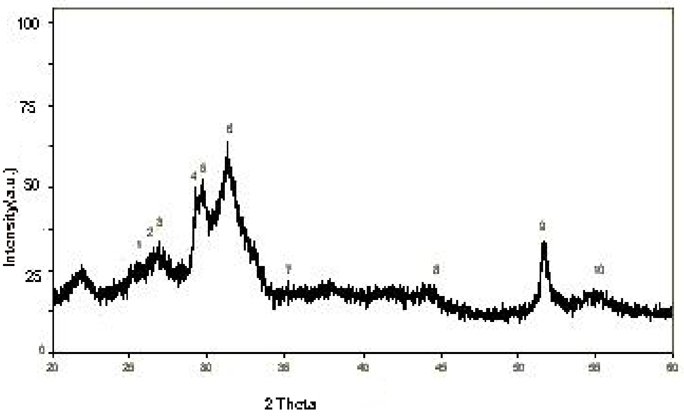

Fig.4. X-ray Diffractogram of CdS$_{0.95}$Se$_{0\cdot 05}$ film with excess sulfur.

On comparing the X-ray diffractograms of the two films (Fig. 3 & 4) we observe that the two films show similar peaks but the intensity of the peaks is decreased in films prepared with excess sulfur. Further the broadening of peaks in this film shows a decrease in the particle size of such films.

The absorption and emission studies are complementary to each other. So both the PL emission spectra and the optical absorption spectra were observed at room temperature for CdS$_x$Se $_{x-1}$ films prepared without and with excess sulfur, shown in Fig. 5 and 6 respectively. The film prepared without excess sulfur showed two broad peaks at ~ 503nm and ~ 575nm while similar films prepared with excess sulfur show similar broad emission peaks at ~ 495nm and 560nm.

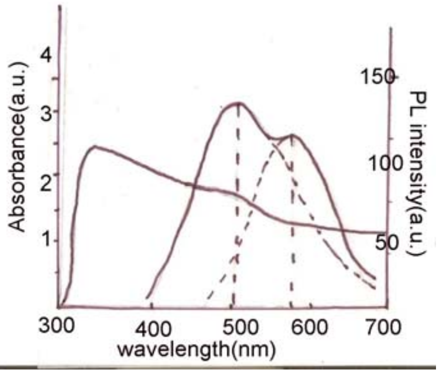

Fig. 5. Optical absorbance and PL emission spectra of a thinner CdS.Se film, prepared without excess sulfur.

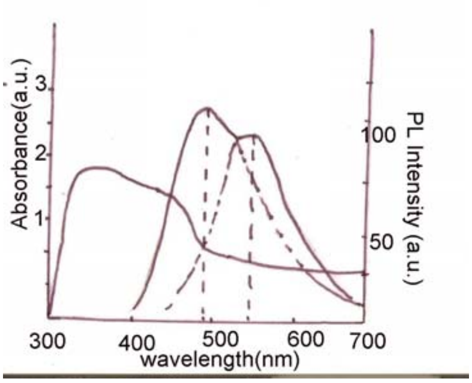

Fig. 6. Optical absorption and PL emission spectra of a thinner CdS-Se film, prepared with excess sulfur.

As observed in the figures these transitions are observed in the vicinity of the band edge. We first try to explain the origin of PL emission peaks observed in the lower wavelength/ higher energy side in both the films namely at ~ 503nm (2.46eV) and at ~ 495nm (2.50eV) for films prepared without and with excess sulfur respectively. Jeong and Yu [7] have recently reported PL in CdS single crystals grown by sublimation method. They observed a broad and intense excitonic emission peak at 2.44eV at 298°K, which was related to annihilation of Ex (A) free exciton and their LO- phonon replica. Owing to the similar excitonic nature of the edge emissions in both CdS and CdSe and also to the fact that for the composition $CdS_{0.70}Se_{0.30}$ in the present case the nature of absorption and emission spectra will be more like those of CdS, the high energy emission peaks observed in both the films can be associated with the annihilation of free excitons. Further, as discussed earlier the films prepared with excess sulfur show broadening of XRD peaks and a shift in the absorption edge towards lower wavelength i.e. higher energy. Both these facts can be related to increase in band gap energy in films prepared with excess sulfur due to decrease in the particle size, which clearly explains the blue shift in the emission peak from 503nm to 495nm in this case. It is well known that these transitions around 490nm in CdS are important as they give rise to laser action under electron beam pumping.

Apart from this it is interesting to note that the difference between the two high energy PL peaks in the films prepared with and without excess sulfur is ~ 40meV. This energy corresponds to longitudinal optical (LO) phonon energy of CdS, so the high energy peak observed in film prepared with excess sulfur may be thought of as a LO phonon replica of that observed in film prepared without excess sulfur or vice-versa. However, the lower energy peaks observed at ~ 575nm (2.15eV) and 560nm (2.21eV) in the two films respectively, shift towards higher wavelength with increasing mol% of Se in both the films (PL spectra of the former film shown in Fig.7).

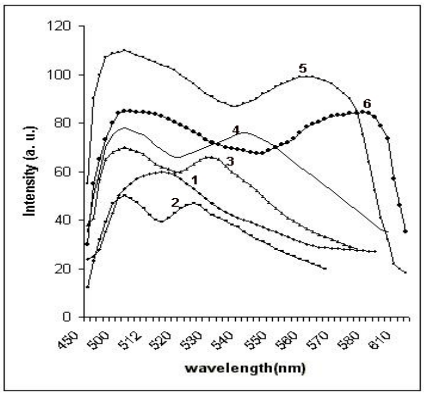

Fig. 7. PL emission spectrum of various CdSxSe1-x films prepared with excess sulfur with variations in x: 1. CdS.2. $CdS_{0.95}Se_{0.05}$. 3. $CdS_{0.90}Se_{0.10}$. 4. $CdS_{0.80}Se_{0.20}$. 5. $CdS_{0.70}Se_{0.30}$. 6. $CdS_{0.60}Se_{0.40}$.

The inclusion of selenium generates new acceptor levels in the lattice. In CdS type materials the incorporation of cations (excess Cd in present case) introduce shallow donor levels (like S vacancies with ionization energies ~ 0.03eV) where as that of anions (S or Se in present case) introduce deep acceptor levels (Cd vacancies, with ionization energy typically ~ 1.1eV for sulfides and ~ 0.6eV for selenides) for the charge compensation of the system [8]. Excess sulfur creates new acceptor levels in the form of Cd vacancies for charge compensation in the lattice. This type of self-compensation by large band gap material is also energetically favourable [9]. In the present method of preparation the excess Cd was produced naturally, which act as donors, where as sulfur and selenium generate acceptors. The variations of peak positions with different concentration of acceptor states with inclusion of more and more sulfur or selenium appear as a natural consequence of inter-impurity transitions between donor and acceptor levels. Similar results were reported by Thomas et al. [10] for the edge emission of CdS.

For studying the variations in PL emission with temperature and excitation intensity, PL measurements are performed in a liquid He continuous flow cryostat in a temperature range from 100 to 300 K. The 404-nm line of a LD is used for the excitation. The PL is spectrally resolved by a monochromator and detected by a cooled CCD array detector. To identify the origin of excitonic peaks, we studied the dependence of the peak emission intensity on the excitation laser density at different temperatures. The intensity of both peaks A and B increases linearly with excitation laser density and a slope (k) near unity is obtained over the whole temperature range. This shows the excitonic origin of the emission [11] that persists up to room temperature.

As shown in Fig.8, the non-monotonic dependence of the PL emission intensity on temperature can be explained by a bound exciton to free exciton transition.

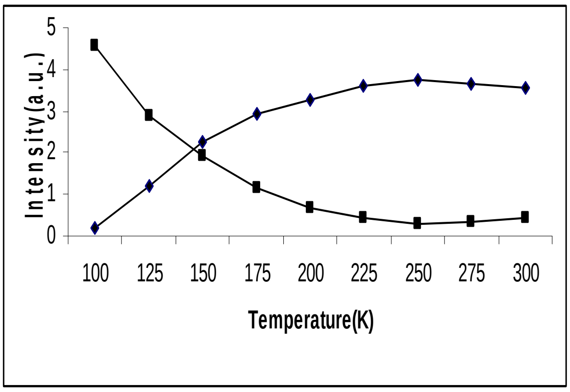

Fig. 8. Temperature dependence of PL emission from bound and ▲free excitonic emission.

At low temperatures, where the bound exciton emission dominates the decrease in emission intensity with increasing temperature is caused by thermal excitation of bound excitons to free excitons. Over the temperature range 100–125 K, the increase in emission intensity is due to the higher free exciton recombination efficiency. At the highest temperatures studied, the decrease in intensity is caused by exciton dissociation, exciton escape from the well to the barriers, and/or the transfer to the nonradiative recombination centers. However, the decrease is small and the room temperature emission intensity is still about 40% of that at 100 K.

4. Conclusions

The excitonic transitions were studied in the PL and optical absorption spectra of chemically deposited CdS_xSe_{x-1} films. The PL emission spectra of the films consisted of two peaks related to annihilation of free excitons and donor-acceptor pair transition. The peak positions in films prepared with excess sulfur were shifted towards lower wavelengths. The optical absorption edge of these films also shows a similar shift in such films. This shift was related to the decrease in particle size and hence a change in the band gap with the incorporation of excess sulfur in the lattice.

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