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Structural and Optical properties of chemically deposited Cd(S-Se):CdCl₂,Sm films

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Structural and Optical properties of chemically deposited Cd(S-Se):CdCl₂,Sm films

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Key words: photoconduction, chemical bath deposition, photoluminescence, energy band gap.

Abstract:

Results of SEM and XRD studies, optical absorption and photoluminescence (PL) emission spectra and photoconductivity (PC) rise and decay studies are reported for Cd(S-Se):CdCl₂,Sm films prepared by chemical deposition method on glass substrates at 60°C in a water bath (WB). SEM studies show ball-type structures along with voids which are related to layered growth. XRD studies show prominent diffraction lines of CdS and CdSe along with some peaks of CdCl₂ and the impurity Sm. The values of strain (ξ), grain size (D) and dislocation density (δ) are evaluated from XRD studies and the nature of crystallinity of the films are discussed. Optical Absorption spectra also show the presence of Sm in the lattice. From the results of optical absorption spectra, the band gaps are determined. PL emission spectra of Cd(S-Se) consist of two peaks which are related to the edge emission of CdS and CdSe involving excitons. In Sm doped emissions

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corresponding to transitions $^4\text{G}_{9/2}$ to $^6\text{H}_{5/2}$, $^6\text{H}_{7/2}$ and $^6\text{H}_{9/2}$ are observed. Sufficiently high photo current ($I_{\text{ph}}$) to dark current ($I_{\text{dc}}$) ratios with a maximum value of the order of $10^6$ are also obtained in some special cases. This high photosensitization is related to increase in mobility and life time of carriers due to photo excitation.
1. Introduction:

II-VI binary semi-conducting 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 band-gap width and sensitive to infra-red part of solar spectrum, good electrical properties (e.g. carrier mobility and life-time) and increased capability in obtaining adjustable n- or p-type conductivity by doping. Particularly, in the visible and near infra-red, direct band-gaps 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(S$_{1-x}$-Se$_x$) (0.1 < x < 1) system (Murali and Venkatachalam 2008).

Impurities, particularly the rare earth 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 (Reisfeld et al 2003). 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, near monochromatic lines in the optical spectra. Furthermore, the f-f transitions are fairly insensitive to conditions such as temperature and the surrounding chemical environment (Ballato et al 1999; Hufner 1978; Denning 2001). Luminescent properties of rare-earth ions together with the large number of available transitions ranging from the deep ultra violet to the mid infra-red make them ideal candidates for optical applications, such as phosphors, lasers, display and amplification systems (Mass et al 2002). Particularly, the energy levels of the emitting
state of Sm ($^4G_{5/2}$), the impurity selected for the present work [approximately 19000 cm$^{-1}$] lies below the energy-level of the trap-states in Cd(S-Se) base, hence energy transfer from host defects to the rare-earth activator Sm$^{3+}$ occurs (Friendel et al 2003) and hence presents an interesting activator.

Several techniques e.g. vacuum evaporation, spray pyrolysis, molecular beam epitaxy etc. (Karanjai et al 1987) were employed for the growth of thin films of the ternary system Cd(S-Se). In this work, Cd(S-Se) films doped with Sm$^{3+}$ ions were deposited by chemical bath deposition method. This is one of the cheapest and simplest techniques for forming films. Chemical deposition techniques for metal chalcogenide semiconductor thin films refer to the deposition of thin films on substrates maintained in contact with dilute chemical bath containing the metal and chalcogen ions (Chopra et al 1982). Bhushan and coworkers (2002; 2006; 2008) used chemical bath deposition (CBD) technique and reported quite high photo-sensitivity, PL, Photovoltaic effect and AC electro-luminescence in such films. The utility of chemical deposition method in metal chalcogenide thin films was reviewed by Mane and Lokhande (2000).

The present paper reports structural and optical properties of Sm$^{3+}$ doped Cd(S-Se) films in terms of SEM, XRD, absorption spectral, PL and PC studies, not explored earlier.

2. Experimental :

Preparation of films : Chemical bath deposition technique was used to deposit films of Cd(S-Se):CdCl$_2$:Sm on glass substrates (cleaned with acetone and double distilled water) of dimensions(24 mm x 75 mm) by dipping vertically into a mixture of solutions of 1M cadmium acetate, appropriate ratio of thiourea and sodium seleno-
sulphate \([\text{Na}_2\text{SeSO}_3]\) solution (prepared by heating elemental selenium (99.9% pure) in aqueous solution of sodium sulphite \([\text{Na}_2\text{SO}_3]\) at 90\(^\circ\)C for 5 hrs.), triethanolamine (TEA) and 30% aqueous ammonia. All the chemicals used were of AR grade. All the solutions were prepared in double distilled water. For preparing doped films, calculated proportions of 0.01M solutions of samarium nitrate and cadmium chloride were added to the original mixture. 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.

TEA 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 mixture were optimized. The optimum time, temperature and pH were observed to be 1 hr., 60\(^\circ\)C and 11.2 respectively. Film thicknesses were determined by optical interference method and were found to lie in the range of 0.4694 - 0.4837 \(\mu\)m. Annealing of the films was done at a temperature of 350\(^\circ\)C for 3 minutes.

The mechanism of deposition of CdS films is based on the slow release of \(\text{Cd}^{2+}\) and \(\text{S}^2-\) ions in aqueous basic solution and subsequent condensation of these ions on the substrates vertically mounted in the solution. The slow release of \(\text{Cd}^{2+}\) ions is achieved by the dissociation equilibrium of a complex species of cadmium \(\text{Cd(TEA)}^2+\).

\[
[(\text{Cd})\text{TEA}]^2+ \leftrightarrow \text{Cd}^{2+} + \text{TEA}
\]

The \(\text{S}^2-\) ions are provided by the dissociation of thiourea \([\text{SC(NH}_2)_2]\) in the ammoniacal medium.

\[
\text{SC(NH}_2)_2 + \text{OH}^- \rightarrow \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{HS}^-
\]

\[
\text{HS}^- + \text{OH}^- \rightarrow \text{S}^2- + \text{H}_2\text{O}
\]
The hydrolysis of sodium seleno-sulphate (Na₂SeSO₃) in the solution to give Se²⁻ ions is according to the chemical reaction (Ezema 2007)

\[ \text{Na}_2\text{SeSO}_3 + \text{OH}^- \leftrightarrow \text{Na}_2\text{SO}_4 + \text{HSe}^- \quad \text{(4)} \]

\[ \text{HSe}^- + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{Se}^{2-} \quad \text{(5)} \]

Similarly, the hydrolysis of ammonia in water to give OH⁻ ion is according to the equation:

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{(6)} \]

When the ammonia is added to the Cd²⁺ salt solution, Cd(OH)₂ starts precipitating, when the solubility-product of Cd(OH)₂ is exceeded.

\[ \text{Cd}^{2+} + 2 \text{OH}^- \leftrightarrow \text{Cd(OH)}_2 \quad \text{(7)} \]

The Cd(OH)₂ precipitate dissolves in excess ammonia solution to form the complex cadmium tetra-amine ions [Cd(NH₃)₄]²⁺.

\[ \text{Cd}^{2+} + 4 \text{NH}_3 \leftrightarrow [\text{Cd(NH}_3)_4]^{2+} \quad \text{(8)} \]

Finally, the deposition of Cd(S-Se) thin film occurs according to the following reaction, when the ionic-product of Cd²⁺ and S²⁻ or Cd²⁺ and Se²⁻ ions in the solutions controls the rate of precipitation and hence the rate of film formation (Kale and Lokhande 2004).

\[ [\text{Cd(NH}_3)_4]^{2+} + \text{S}^{2-} + \text{Se}^{2-} \leftrightarrow \text{Cd(S-Se)} + 4 \text{NH}_3 \quad \text{(9)} \]

Role of CdCl₂ in the film formation is two fold : (i) it helps in re-crystallization of the base material and (ii) it acts as a flux for incorporation of impurity in the base material.
The growth mechanism of thin films using chemical bath deposition (CBD) method can take place either in the bulk of the solution (homogeneous precipitation process) or at the substrate surface (heterogeneous process). It can be considered as 'cluster by cluster' growth, leading to the particulate films. The latter is a growth mechanism involving the reaction of atomic species at the surface, it corresponds to an atom by atom process, also called "ion by ion" process (Kaur et al. 1980).

**PL and PC Cells**: The PL cell consisted of the film deposited on the substrates. For PC studies, coplanar electrodes (1.5 mm wide and 24 mm long at a separation of 2 mm) were formed by applying colloidal silver paint to the surface of the film. The photocurrents were measured by exposing the total area of the film.

3. Results and discussion:

**SEM studies**: The SEM micrographs of Cd(S-Se):CdCl₂,Sm films chemically deposited on glass substrate at 60°C in WB and their annealed samples are presented in figure-1(a), (b), (c) and (d) respectively. Ball type structure along with some voids are observed. 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.
XRD studies: The X-ray diffractograms of Cd(S-Se):CdCl₂,Sm films chemically deposited on glass substrate at 60°C in WB and their annealed samples are presented in figure-2(a), (b), (c) and (d) respectively. The corresponding data are presented in table 1.
The assignments of peaks were made by comparing with ASTM data, and calculation of lattice constants and their comparison with the reported values. The different assigned peaks are mentioned in the figures. Thus, prominent peaks of CdS \{((111)_h, (101)_h, (200)_h, (220)_h, (112)_h and (102)_h}\) and CdSe \{(100)_h, (002)_h and (110)_h\} along with two peaks of Sm \{(101)_h and (104)_h\} and one peak of CdCl₂ \{(021)_h\} are observed.
The intensities of (111)\(c\) peak of CdS and (100)\(h\) peak of CdSe are dominant. Existence of Sm and CdCl\(2\) are also found.

Table 1  XRD data of different chemically deposited Cd(S-Se):CdCl\(_2\),Sm films on glass substrate at 60\(^\circ\)C in WB

<table>
<thead>
<tr>
<th>d-values</th>
<th>Relative Intensities</th>
<th>hkl</th>
<th>Lattice-constants (Å(^8))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>Rep.</td>
<td>Obs.</td>
</tr>
<tr>
<td>(a) Cd(S(<em>{0.85})-Se(</em>{0.15})):CdCl(_2),Sm (3ml)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.7245</td>
<td>3.7230</td>
<td>91.3</td>
<td>100</td>
</tr>
<tr>
<td>3.5010</td>
<td>3.51</td>
<td>93.2</td>
<td>65.85</td>
</tr>
<tr>
<td>3.3609</td>
<td>3.36</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3.181</td>
<td>3.16</td>
<td>86.2</td>
<td>100</td>
</tr>
<tr>
<td>3.0919</td>
<td>3.09</td>
<td>86.9</td>
<td>30</td>
</tr>
<tr>
<td>2.8173</td>
<td>2.81</td>
<td>82.5</td>
<td>40</td>
</tr>
<tr>
<td>2.9015</td>
<td>2.9</td>
<td>69.05</td>
<td>40</td>
</tr>
<tr>
<td>2.1542</td>
<td>2.15</td>
<td>45.5</td>
<td>82.43</td>
</tr>
<tr>
<td>2.0404</td>
<td>2.06</td>
<td>47.7</td>
<td>57</td>
</tr>
<tr>
<td>1.7616</td>
<td>1.76</td>
<td>42.5</td>
<td>45</td>
</tr>
<tr>
<td>1.658</td>
<td>1.658</td>
<td>40.73</td>
<td>12</td>
</tr>
<tr>
<td>(b) Cd(S(<em>{0.85})-Se(</em>{0.15})):CdCl(_2),Sm (2ml)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.7227</td>
<td>3.7239</td>
<td>91.74</td>
<td>100</td>
</tr>
<tr>
<td>3.5224</td>
<td>3.52</td>
<td>98.08</td>
<td>65.85</td>
</tr>
<tr>
<td>3.3685</td>
<td>3.36</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3.0999</td>
<td>3.09</td>
<td>88.79</td>
<td>30</td>
</tr>
<tr>
<td>2.8283</td>
<td>2.81</td>
<td>83.33</td>
<td>40</td>
</tr>
<tr>
<td>2.6905</td>
<td>2.68</td>
<td>76.69</td>
<td>40</td>
</tr>
<tr>
<td>2.4501</td>
<td>2.4502</td>
<td>56.49</td>
<td>25</td>
</tr>
<tr>
<td>2.3194</td>
<td>2.345</td>
<td>47.19</td>
<td>100</td>
</tr>
<tr>
<td>2.1705</td>
<td>2.15</td>
<td>44.54</td>
<td>82.43</td>
</tr>
<tr>
<td>1.7757</td>
<td>1.76</td>
<td>39.08</td>
<td>45</td>
</tr>
<tr>
<td>1.659</td>
<td>1.658</td>
<td>38.05</td>
<td>12</td>
</tr>
<tr>
<td>(c) Cd(S(<em>{0.85})-Se(</em>{0.15})):CdCl(_2),Sm (3ml)[annealed]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.7294</td>
<td>3.7239</td>
<td>52.17</td>
<td>100</td>
</tr>
<tr>
<td>3.335</td>
<td>3.36</td>
<td>94.85</td>
<td>100</td>
</tr>
</tbody>
</table>
Different layers of CdS are observed in cubic as well as hexagonal phases. The formation of the hexagonal and cubic phases are known to be created through different arrangements of atomic layers. The hexagonal phase consists of the sequence of atomic layers defined as ABABAB----- and that of cubic in ABCABCABC----- (Kittel 1995). It is also possible to find mixed forms with random stacking of very long period repeats as is found in polytypes of SiC (Ibach and Lüth 1991). The total crystal consists of different atomic layers of CdS in cubic as well as hexagonal phases along with some atomic layers of CdSe in hexagonal phases. According to Langer et al (1996), one might think of solid solutions as mixtures of microcrystalline regions of the pure CdSe and CdS, where each microregion might consist of a number of unit cells of each material with the lattice-
constant of CdS stressed by surrounding CdSe and that of CdSe compressed by its CdS neighbours. 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. It should be noted that shift of absorption edge has already been observed in the present case.

Table 2: Values of FWHM, Particle size, Strain and Dislocation density corresponding to (111)c peak of CdS for different chemically deposited Cd(S-Se):CdCl₂,Sm films on glass substrate at 60°C in WB

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM 'θ' (radian)</th>
<th>Particle Size 'D' (nm)</th>
<th>Strain 'ε' (10⁻²³ nm⁻²)</th>
<th>Dislocation Density 'δ' (x10⁻¹³ nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(S₀.₉₇-Se₀.₀₃):CdCl₂,Sm(3 ml)</td>
<td>0.033</td>
<td>33</td>
<td>0.0114</td>
<td>0.59</td>
</tr>
<tr>
<td>Cd(S₀.₇-Se₀.₃):CdCl₂,Sm(2 ml)</td>
<td>0.022</td>
<td>58</td>
<td>0.0058</td>
<td>0.335</td>
</tr>
<tr>
<td>Cd(S₀.₉₅-Se₀.₀₅):CdCl₂,Sm(3ml) [annealed]</td>
<td>0.015</td>
<td>45</td>
<td>0.0084</td>
<td>0.130</td>
</tr>
<tr>
<td>Cd(S₀.₇-Se₀.₃):CdCl₂,Sm(2ml) [annealed]</td>
<td>0.017</td>
<td>86</td>
<td>0.0039</td>
<td>0.135</td>
</tr>
</tbody>
</table>

The particle size D (Wilson 1963), strain value ε (Senthilkumar et al 2005) and dislocation density δ (Williamson and Smallman 1956) were obtained for (111)c peak of CdS by using the well known formulae and corresponding values are listed in table-2. It is noticed that with annealing of films; FWHM, strain value and dislocation density decrease, whereas the particle-size increases. The decrease in dislocation density suggests that films become more crystalline. Annealing of thin films increases the grain size resulting in better crystallinity.

Optical absorption spectra: The optical absorption measurements of the Sm doped Cd(S-Se) films were carried out at room temperature by placing an uncoated
identical glass substrate in the reference beam. The optical spectra of the films were recorded in the wavelength range 300-700 nm. The energy band gaps of the materials in these films were determined from the absorption spectra.

Fig.-3(a) Absorption spectrum of Cd(S$_{0.95}$-Se$_{0.05}$)-film

Fig.-3(b) Absorption spectrum of Cd(S$_{0.95}$-Se$_{0.05}$):CdCl$_2$(3ml)-film

Fig.-3(c) Absorption spectrum of Cd(S$_{0.95}$-Se$_{0.05}$):CdCl$_2$(3ml),Sm(3ml)-annealed film

Fig.-3(d) Absorption spectrum of Cd(S$_{0.7}$-Se$_{0.3}$):CdCl$_2$(2ml),Sm(2ml)-film
The optical absorption spectra of CdS and different Cd(S-Se) films prepared on glass substrates are shown in figure-3. Band gaps were determined from the extrapolation of the plots between \((ahv)^2\) vs \(hv\) (Tauc's plots) (fig.-4). It is found that with increase in concentration of CdSe the band gap decreases [Cd(S0.95-Se0.05): 2.36 eV; Cd(S0.9-Se0.1): 2.33 eV; Cd(S0.8-Se0.2): 2.26 eV; Cd(S0.7-Se0.3): 2.19 eV; Cd(S0.6-Se0.4): 2.12 eV]. A plot of \(E_g\) versus CdS/CdSe ratio is shown in fig.-5. This shows that a common lattice of Cd(S-Se) is formed through the solid solution formation. Slight changes in band gaps are observed in presence of CdCl\(_2\) and Sm. The overall absorption in presence of Se and Sm decrease which shows that the films become more transparent in their presence. The spikes observed at around 300 nm may also occur due to nano-crystalline effects under which the continuum of states in conduction band (CB) and valence band (VB) are broken into discrete states (Efros and Efros 1982).

Also, in Sm doped film, a weak absorption peak is observed at around 404 nm. Li Yu Chun et al (2007) have shown that, after excitation with wavelengths 404 nm corresponding to the direct excitation from ground \(^6\)H\(_{5/2}\) to higher energy levels dominant excitation to \(^4\)K\(_{11/2}\) states of Sm\(^{3+}\) ion, the emission spectrum is dominated by Sm\(^{3+}\).
luminescence mainly in the orange-red region which are assigned to the intra-4f-shell transition from the excited level $^4G_{5/2}$ to the lower levels $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$.

**PL Emission Spectra**: Maximum PL emission is observed for 0.7:0.3 combination of CdS:CdSe and hence this combination was used for PL studies. In the presence of flux, at its different concentrations, the highest emission appears at a volume of 2 ml CdCl$_2$. Therefore, this concentration was used in the presence of impurities. Plots of PL intensity versus wavelength for CdS and different Cd(S-Se) films are shown in fig.-6(a) and 6(b) respectively; and those for varying volumes of Sm$^{1+}$ are shown in fig.-7. The corresponding peak positions are mentioned in table-3.

![Fig.-6 PL emission spectra of different Cd(S$_{1-x}$-Se$_x$) films prepared at 60°C with different values of $x$: □ CdS, ○ Cd(S$_{0.7}$-Se$_{0.3}$), ▲ Cd(S$_{0.2}$-Se$_{0.8}$), ▼ Cd(S$_{0.7}$-Se$_{0.3}$) and ◆ Cd(S$_{0.8}$-Se$_{0.2}$) ]

![Fig.-7 PL emission spectra of Cd(S$_{0.7}$-Se$_{0.3}$):CdCl$_2$(2ml),Sm(2ml) films prepared on glass substrates at 60°C at different volumes of Sm(NO$_3$)$_3$ (0.01M): □ 2ml, ○ 4ml, ▲ 6ml, ▼ 8ml, ♦ 10ml and ◆ 12ml.]

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Fig. 8 Deconvolution of PL emission spectrum of \( \text{Cd(S}_{0.7-\text{Se}_{0.3}} \) into Gaussian curves

Table 3 Values of peak positions of CdS and different chemically deposited Cd(S-Se) films on glass substrate at 60°C in WB

<table>
<thead>
<tr>
<th>Systems</th>
<th>Peak Positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CdS</td>
<td>511</td>
</tr>
<tr>
<td>2. Cd(( \text{S}<em>{0.95-\text{Se}</em>{0.05}} ))</td>
<td>494, 516</td>
</tr>
<tr>
<td>3. Cd(( \text{S}<em>{0.9-\text{Se}</em>{0.1}} ))</td>
<td>494, 525</td>
</tr>
<tr>
<td>4. Cd(( \text{S}<em>{0.8-\text{Se}</em>{0.2}} ))</td>
<td>494, 542</td>
</tr>
<tr>
<td>5. Cd(( \text{S}<em>{0.7-\text{Se}</em>{0.3}} ))</td>
<td>494, 559</td>
</tr>
<tr>
<td>6. Cd(( \text{S}<em>{0.6-\text{Se}</em>{0.4}} ))</td>
<td>494, 577</td>
</tr>
<tr>
<td>8. Cd(( \text{S}<em>{0.7-\text{Se}</em>{0.3}} )):CdCl(_2) (2 ml), Sm(2ml)</td>
<td>563, 595, 614</td>
</tr>
</tbody>
</table>

PL emission spectrum of CdS was found to consist of a peak at 511 nm. This emission is quite close to the band gap as obtained from the absorption spectrum. Thus,
This may be due to the edge emission of CdS. This edge emission was attributed to the excitonic transitions involving free excitons (Thomas and Hopfield 1962). The peak positions of emission spectra of CdS and Cd(S-Se) are presented in table-3. The peak positions in Cd(S-Se) at different compositions of S and Se were obtained by deconvolution into Gaussian curves and for one composition, these peaks are shown in fig.-8. The peak observed at 516 nm for Cd(S$_{0.95}$Se$_{0.05}$) shows a shift towards higher wavelength with increasing concentration of Se. This emission, thus, can be identified as the edge emission of Cd(S-Se). Owing to similar excitonic nature in both CdS and CdSe, this emission can be attributed to the radiative decay of the free exciton. The peak at 494 nm may be attributed to the exciton bound to neutral donor levels formed by sulphur / excess Cd (Bhushan and Oudhia 2008). Higher volumes of sodium seleno sulphate (Na$_2$SeSO$_3$) were added for increasing the concentration of CdSe. Thus, the formation of more sulphur could be expected, enhancing the emission in its presence (Bhushan and Oudhia 2008). A prominent peak at 505 nm in Cd-rich single crystals of CdS at room temperature was also reported by Kokubun et al (Kokubun and Kaeriyama 1975). Further, the possibility of shift of emission peak due to nano-crystalline effect cannot be ignored. Thus, the 494 nm peak may be due to the shift of bulk emission of CdS at 511 nm and the 559 nm peak may be due to the shift in peak position of CdSe at 712 nm. In presence of Sm, along with the peak at 494 nm, the other peaks observed are at 563 nm, 595 nm and 614 nm respectively. These peaks may be associated to the transitions from the excited level $^4$G$_{5/2}$ to ground levels $^6$H$_{5/2}$, $^6$H$_{7/2}$ and $^6$H$_{9/2}$ respectively \{ $^4$G$_{5/2}$ $\rightarrow$ $^6$H$_{5/2}$, $^4$G$_{5/2}$ $\rightarrow$ $^6$H$_{7/2}$ and $^4$G$_{5/2}$ $\rightarrow$ $^6$H$_{9/2}$ \} [fig.-9].
PC rise and decay studies: The PC rise and decay curves of different Cd(S-Se) films prepared on glass substrates are shown in fig. 10. It is observed that when light is illuminated on the film, the photocurrent first increases rapidly due to generation of e-h pairs through absorption of photons by the materials of the films mostly from the surface region of the film. The rate of increase of photocurrent decreases with time due to recombination of carriers and after some time, the photocurrent is almost constant due to a balance between the generation and recombination i.e. resulting in saturated value of current. When light is turned off, photocurrent decreases very rapidly and after a few seconds, it decreases steadily with respect to time. Here surface recombination is very high and it leads to a lower carrier concentration at the surface. The system tends to its initial stage by relaxation process, which gives low and steady decay of photocurrent.
Fig. - 10. PC rise and decay curves of different Cd(S-Se) films prepared on glass substrates at 60°C: □ Cd(S_{0.95-Se_{0.05}}), ○ Cd(S_{0.95-Se_{0.05}}):CdCl₂, ▲ Cd(S_{0.95-Se_{0.05}}):CdCl₂,Sm(3ml) and ▼ Cd(S_{0.95-Se_{0.05}}):CdCl₂,Sm(3ml) [annealed].

Maximum photocurrent was observed in the case of 0.95:0.05 combination of CdS to CdSe. In the presence of CdCl₂, the maximum current was observed for a volume of 3 ml (0.001M). The values of Iᵢp/Iᵢc ratio, trap-depths, instantaneous lifetime and mobility were evaluated by methods described in earlier publications (Bhushan et al 2001) and the corresponding values for the different cases are summarized in the table-4.

Table 4: Values of Iᵢc, Iᵢp, Iᵢp/Iᵢc, Lifetime (τ), Mobility (μ) and Trap depth (E) for different Cd(S-Se) films. (Temp. of preparation = 60°C; duration = 1hr)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample</th>
<th>Iᵢc (nA)</th>
<th>Iᵢp (μA)</th>
<th>Gain</th>
<th>Iᵢp/Iᵢc</th>
<th>Lifetime (sec)</th>
<th>Mobility (cm²/Ns)</th>
<th>Trap depth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cd(S_{0.95-Se_{0.05}})</td>
<td>0.2</td>
<td>134</td>
<td>6.7x10⁻³</td>
<td>39.41</td>
<td>45.33</td>
<td>E₁=0.673,E₂=0.665</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cd(S_{0.95-Se_{0.05}}):CdCl₂</td>
<td>0.1</td>
<td>264</td>
<td>2.64x10⁶</td>
<td>48.01</td>
<td>93.33</td>
<td>E₁=0.684,E₂=0.668</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cd(S_{0.95-Se_{0.05}}):CdCl₂,Sm</td>
<td>0.05</td>
<td>402.41</td>
<td>8.05x10⁶</td>
<td>61.9</td>
<td>148.19</td>
<td>E₁=0.696,E₂=0.679</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>at 60°C in WB</td>
<td>-0</td>
<td>54.2</td>
<td>very high</td>
<td>67.4</td>
<td>Very high</td>
<td>E₁=0.699,E₂=0.681</td>
<td></td>
</tr>
</tbody>
</table>

19
It is observed that, the values of lifetime and mobility both increase in the presence of impurities, which accounts for the better photo-response.

4. Conclusions: SEM studies of the chemically deposited Sm doped Cd(S-Se) films show ball type structures, which may be due to layered growth. X-ray diffractograms of Cd(S-Se):CdCl₂,Sm films show the presence of CdS and CdSe along with some peaks of CdCl₂ and Sm. From the calculation of strain and dislocation density, crystallinity is found to be better in RT preparation. PL emission spectra of the doped films consist of peaks due to transitions in impurity levels. PC rise and decay studies show \( I_{pc}/I_{dc} \) ratio of the order of \( 10^6 \). Such higher photosensitization occurs due to increase in life-time and mobility of carriers.

Acknowledgements: The authors are grateful to IUC-DAE, Indore (M.P.) for giving consent for completing SEM and XRD studies at the consortium. One of the authors (R.S.S.) is thankful to the University Grants Commission, New Delhi for the award of a Teacher Fellowship under 10th plan.

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Dear Sir,

I am happy to inform you that your paper entitled "Photoluminescence and Photoconductivity in Lanthanide Doped Chemically Deposited CdS-Se Films" has been accepted for the NCLA-2009 going to be held at CGCRI, Kolkata during 19-21 Feb, 2009.

Looking forward to meet you at Kolkata.

With regards,
R. Debnath
Convener, NCLA-2009
Photoluminescence and Photoconductivity in Lanthanide Doped Chemically Deposited CdS-Se Films

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Abstract

Some interesting results of photoluminescence (PL) and photoconductivity (PC) observed in chemically deposited films of lanthanide doped CdS-Se are presented in this talk. Strong PL and high photosensitization are observed at particular concentrations of the two bases. An edge emission corresponding to radiative decay of the free exciton and a broad green emission related to exciton-donor complexes formed in presence of excess Cd are observed in the PL emission spectra of various CdS-Se films. In doped films, characteristic emissions of lanthanides such as Ho and Sm are observed. Some properties related to nanocrystalline effects are also found. Results of optical absorption spectra also support such observations i.e. apart from host absorption, absorption due to impurities are observed. High photosensitization has also been observed under some special conditions. Results of XRD confirm the presence of CdS and CdSe. SEM studies show growth of layered structure. All these interesting observations form the subject of this invited talk.

INTRODUCTION

The wide technological applications of CdS type materials make the PL and PC studies important. Some of the important applications of PL are lamp phosphors and display devices and those of PC are xerography and IR detectors 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]. Similarly PC of CdS and CdSe were extensively studied by Bube and co-workers [5,6]. The effect of alloying of CdS, CdSe and other II-VI group compounds on the PL and PC properties has attracted the interest of research workers in recent years. Regarding the PL spectral studies of CdS-Se, Shevel et al [7] studied the localized electronic states created by the compositional disorder in CdS-Se employing the pico-second luminescence spectral studies. Pagliara et al [8] correlated the structural disorders in CdS,Se1-x to localization of excitons observed in PL spectra. Regarding PC studies Gupta et al [9] reported PC studies in CdS,Se1-x evaporated layers and used grain-boundary– trapping model to determine the barrier height at the inter-crystalline boundary. Further, application of high speed chemically deposited CdS0.2Se0.80 photoconductor as line image sensors and superior stability were reported by Yukami et al [10] and Rincon et al [11] respectively. Encouraged with such
results, CdS-Se was selected as the base material for the present studies. Bhushan and coworkers [12-15] found enhancement in PL and PC due to doping of lanthanides in (Cd-Zn)S and (Cd-Pb)S. So for the present work Ho and Sm were selected as impurities. While Ho can be expected to sensitize PL due to its well separated energy levels, it can also help in PC due to valence electrons. Inorganic compounds using Ho as impurity have got important applications in luminescent devices like luminescent lamps, cathode ray tubes and lasers [16]. Further, reason for selecting Sm has been the energy levels of its emitting state $^4G_52$ 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 [17] and hence presented interesting activator.

The present paper reports results of PL emission spectra, PC rise and decay, absorption spectra, XRD and SEM studies of chemically deposited films of Ho and Sm doped CdS-Se.

**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, thiourea, tri-ethanolamine, 0.01 M solutions of cadmium chloride, holmium oxide / samarium nitrate and 0.42 M solution of sodium selenosulphate in appropriate proportions in presence of 30% aqueous ammonia. Being insoluble in water, solution of holmium oxide was prepared in sulphuric acid; solutions of all other chemicals were prepared in double distilled water. The pH value of the mixture was ~ 9. After deposition the films were sprayed 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 0.1 to 0.9 μm.

For PC measurements coplanar colloidal silver paint electrodes of 1.5 mm width and 24 mm length were formed at a separation of 2 mm. The PL cell consisted of films deposited on the substrates. An incandescent bulb of 100 W was used as excitation source for PC growth and decay studies. 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:2H2R horizontal Rotaflex and JEOL-JSM 5600 respectively.

**RESULTS AND DISCUSSIONS**

**SEM Studies :**

The SEM micrographs of CdS$_{0.70}$Se$_{0.30}$ and CdS$_{0.95}$Se$_{0.05}$ films are shown in fig. 1 and 2 respectively. These configurations correspond to maximum PL and PC response respectively. A leafy structure is observed in both the figures which may appear due to layered growth of the films. The thickness of the layers lie in the nano-range. A similar
nature along with some micro-crystallites spread over the leafy structure are found in doped films.

Fig. 1 SEM micrograph of CdS$_{0.95}$Se$_{0.05}$ film

Fig. 2 SEM micrograph of CdS$_{0.70}$Se$_{0.30}$ film

**XRD Studies:**

Fig. 3 shows the X-ray diffractogram of CdS$_{0.95}$Se$_{0.05}$ film. The assignment of peaks have been made by using JCPDS data and comparing the evaluated values of lattice constants with those of the reported values. Thus, prominent peaks of CdS and CdSe are observed.

Fig. 3 X-ray diffractogram of CdS$_{0.95}$Se$_{0.05}$ film; peak
1: (111)$_h$CdS, 2: (101)$_h$CdS, 3: (101)$_h$CdSe, 4: (200)$_h$CdS, 5: (102)$_h$CdSe, 6: (102)$_h$CdS, 7: (110)$_h$CdSe, 8: (220)$_h$CdS, 9: (311)$_h$CdS, 10: (222)$_h$CdS.

Fig. 4 X-ray diffractogram of CdS$_{0.95}$Se$_{0.05}$:CdCl$_2$:Ho film; peak
1: (002)$_h$CdSe, 2: (111)$_h$CdS, 3: (002)$_h$CdS or (101)$_h$CdCl$_2$, 4: (222)$_h$Ho$_2$O$_3$, 5: (101)$_h$CdSe, 6: (200)$_h$CdS, 7: (102)$_h$CdSe, 8: (220)$_h$CdS, 9: (311)$_h$CdS, 10: (222)$_h$CdS.

Fig. 5 X-ray diffractogram of CdS$_{0.70}$Se$_{0.30}$:CdCl$_2$:Ho film; peak
1: (100)$_h$CdSe, 2: (101)$_h$CdSe, 3: (101)$_h$CdS, 4: (200)$_h$CdS, 5: (102)$_h$CdSe or (400)$_h$H$_2$O$_3$, 6: (102)$_h$CdS, 7: (110)$_h$CdSe, 8: (311)$_h$CdS, 9: (222)$_h$CdS.
The X-ray diffractograms of CdS$_{0.95}$Se$_{0.05}$:CdCl$_2$,Ho and CdS$_{0.70}$Se$_{0.30}$:CdCl$_2$,Ho films are shown in fig. 4 and 5 respectively. From these diagrams along with prominent peaks of CdS and CdSe, some lines of CdCl$_2$ and Ho are also seen. The X-ray diffractograms of Sm doped films are shown in fig. 6 and 7 and in both some lines of Sm are also assigned.

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...[18]. It is also possible to find mixed forms with random stacking of very long period repeats as is found in polytypes of SiC [19]. The total crystal consists of different atomic layers of CdSe in hexagonal phases. According to Langer et al [20], 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. It is worth noting that shift of absorption edge has been observed in the present case.

Absorption Spectral Studies:

Fig. 8 shows optical absorption spectra of different CdS-Se films. The films prepared with different mole % of S and Se show variation in the band gap over different compositional range (e.g. CdS : 2.42 eV; CdS$_{0.40}$Se$_{0.60}$ : 2.13 eV) indicating the formation of a common lattice of CdS-Se through solid solutions. Curves 1 and 2 represent the optical absorption spectra of CdS$_{0.95}$Se$_{0.05}$ and CdS$_{0.70}$Se$_{0.30}$ films respectively. A steep increase in the absorption corresponding to the onset of band-to band transition is observed in both the curves. Further, the optical absorbance decreases in presence of impurity as is shown for Ho doped films in curves 3 and 4 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 decreases. A narrower and resolved absorption peak correspond to narrower size distribution. A blue shift in absorption edges and the energies corresponding to the onset of direct band-to-band transition in Ho doped films prepared with 90% aqueous ammonia (curves 5 and 6) compared to those of films prepared with 30% aqueous ammonia suggests a decrease in particle size. It is known that in nanocrystalline 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. The optical absorption of Ho doped films a hump is observed in 425-525 nm region corresponding to absorption related to transition $^5H_{11/2} \rightarrow {}^5{F}_3$ in Ho [21]. Similarly in Sm doped films a hump at around 404 nm (curve 7) corresponds to $^6{H}_{5/2} \rightarrow {}^4{F}_{11/2}$ transition in Sm$^{3+}$ [22].

**PL Emission Spectra:**

Fig. 9 shows PL emission spectra of CdS and CdS-Se films at different compositions of S and Se. The emission spectrum of CdS shows a peak at 515 nm and those of CdS-Se films show two peaks. The emission peak at 515 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 [23] attributed the edge emission to transitions associated with donor / acceptor exciton complexes. Jeong and Yu [24] 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 [25]. In the present studies, two broad peaks are observed in CdS-Se. The peak observed at ~ 525
nm shows a shift towards higher wavelengths 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 503 nm remains unchanged and may be attributed to excitons bound to neutral donor levels formed by sulphur / 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. In Ho doped films, emissions observed at 495 nm and 545 nm are related to transitions $^5F_3 \rightarrow ^5I_8$ and $^3S_2 \rightarrow ^3I_8$ [21]. Similarly, in Sm doped films emissions corresponding 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 [22].

**PC Studies:**
The PC growth and decay curves for different CdS-Se films are shown in fig. 10. In all such curves, a rapid rise in photocurrent results due to generation of carriers. After this initial rise, when recombination starts becoming effective, the rate of rise becomes slower and finally a balance between the two effects make the current saturated. The decay curves consist of initially a fast decrease followed by a slow decrease. While fast decrease is related to direct recombination effects and the slow decrease is related to release of trapped electrons from deep traps formed in CdS-Se. Parameters like life-time, mobility and trap depths were obtained by methods published elsewhere [12] and are listed in table-1. From these values it is inferred that high photosensitization in such materials is observed due to increase in lifetime, mobility and carrier concentration.

![PC rise and decay curves for different CdS-Se films](image)

**CONCLUSIONS**
The chemically deposited CdS-Se films show layered growth morphology in the SEM studies. In XRD studies, existence of CdS, CdSe, CdCl₂ and impurities are found. PL emission of such films show two peaks in absence of impurities. Presence of impurities are found in terms of transitions in these elements. Absorption studies also support their existence. Such studies also show reduction in band gap due to increasing concentrations of CdSe. At a particular concentration, higher values of photosensitizations are also observed.

ACKNOWLEDGEMENTS

The authors are grateful to IUC-DAE, Indore (M.P.) for SEM and XRD studies and to UGC, ND for providing teacher fellowships to two of them (A.O. and R.S.S.).

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Dear Sir,

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With regards,

R. Debnath
Convener, NCLA-2009
Photoluminescence Studies in chemically deposited Cd(S-Se):CdCl₂:Sm films

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Abstract:
Photoluminescence (PL) emission spectra of chemically deposited Cd(S-Se) films consist of two peaks at 494 and 559 nm which are related to the radiative decay of free exciton and exciton-donor complexes found in the presence of S/excessCd respectively. In Sm doped films, three new peaks appear at 563, 595 and 614 nm, which may be related to the transitions in Sm levels. SEM, XRD and optical absorption spectra of the Cd(S-Se):CdCl₂, Sm film are reported.

Key words: Photoluminescence, chemical bath deposition, energy band gap, x-ray diffraction.

1. Introduction:
PL studies on CdS type materials are important because of their applications as lamp phosphors and display devices etc. When rare earth ions are incorporated into a solid, they show distinct spectral lines of absorption and emission, as a result of the electronic transitions within the 4f shell configuration [1]. Although preparation of CdS films were reported by a variety of techniques e.g. vacuum evaporation, spray pyrolysis, molecular beam epitaxy etc. [2], the chemical deposition technique has drawn interest of a number of workers. Blushan and coworkers [3-6] used chemical deposition technique and reported quite high photo-sensitivity, PL, Photovoltaic effect and AC electro-luminescence in such films. The utility of chemical deposition method in metal chalcogenide thin films was reviewed by Mane and Lokhande [7]. Since Cd(S-Se) has advantage over CdS in changing the band gap of the material, in the present work films of mixed system Cd(S-Se) doped with Sm³⁺ have been prepared using chemical deposition technique. CdCl₂ has been used as flux which also helps in re-crystallization of Cd(S-Se).

In the present paper, along with PL studies results of various characterization studies such as SEM, XRD and absorption spectra are reported for Cd(S-Se):CdCl₂,Sm films and the corresponding results are discussed.

2. Experimental:
Preparation of films: Chemical bath deposition technique was used to deposit films of Cd(S-Se):CdCl₂,Sm on cleaned glass substrates of dimensions (24 mm x 75 mm) which were dipped vertically into a mixture of solutions of 1M cadmium acetate, appropriate ratio of thiourea and sodium seleno-sulphate [Na₂SeSO₃] solution { prepared by heating elemental selenium (99.9% pure) in aqueous solution of sodium sulphite [Na₂SO₃] at 90°C for 5 hrs.}, triethanolamine and 30% aqueous ammonia. For preparing doped films, calculated proportions of 0.01M solutions of samarium nitrate and cadmium chloride were added to the original mixture. The pH of the solution was observed to be 11.2.

Experimental Details: The SEM and XRD studies were made at IUC-DAE Indore, using JEOL JSM-5600 and 3 kW X-ray generator with Cu target respectively. Absorption spectra were studied using Schimadzu UV-VIS 1700 Pharmaspec Spectrophotometer. PL studies were performed under excitation of 365 nm Hg radiation and PL intensities were recorded using RCA 6217 photomultiplier tube. For PL emission spectral studies, a prism monochromator was used.

3. Results and discussion:

SEM studies: The SEM micrograph (at 10K magnification) of Cd(S-Se):CdCl₂,Sm film chemically

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deposited on glass substrate at RT is presented in figure-1. Ball type structure along with some voids is observed. This kind of structure probably appears due to layered type growth of the material, which under continued deposition forms such structure.

XRD studies: The X-ray diffractogram of Cd(S-Se):CdCl₂,Sm film chemically deposited on glass substrate at RT are presented in figure-2.

The assignments were made by comparing with ASTM data, and calculation of lattice constants and their comparison with the reported values. The different assigned peaks are mentioned in the figures. The intensities of (111), peak of CdS and (100), peak of CdSe are dominant.

Optical absorption spectra: The absorption measurements of the Sm doped Cd(S-Se) film has been carried out at RT by placing an uncoated identical glass substrate in the reference beam.

The optical absorption spectrum of the Cd(S-Se) films prepared at RT recorded in the wavelength range 300-700 nm is shown in figure-3 with absorbance (arb. units) on ordinate and wavelength (nm) on abscissa.

Band gap (E_g) of the Cd(S-Se):CdCl₂,Sm film has been determined from the extrapolation of the curve obtained between (ahv)² vs hv. It is found that with increase in concentration of CdSe the band gap decreases as follows:

• Cd(S₀.₉₃-Se₀.₀₇): 2.36 eV;
• Cd(S₀.₇-Se₀.₃): 2.26 eV;
• Cd(S₀.₅-Se₀.₅): 2.12 eV.

A plot of E_g versus CdS/CdSe ratio is shown in fig.-4.

On addition of CdCl₂, there is a slight change in band gap [2.37 eV for Cd(S₀.₉₃-Se₀.₀₇) and 2.25 eV for Cd(S₀.₇-Se₀.₃)]. It has been found that the absorption spectra of Cd(S-Se):CdCl₂,Sm films show an overall decrease in absorption as compared to those of Cd(S-Se) and Cd(S-Se):CdCl₂ films. Thus, the films become more transparent in presence of Sm.

However, the value of band gap obtained from their Tauc's plot [15] is similar (2.39 eV). Also, on Sm doped film, a weak absorption peak is observed at around 404 nm.

PL Emission Spectra: PL emission spectra of CdS and Cd(S-Se) (for various combinations of S and Se) are presented in fig. 5 and 6 respectively. PL emission spectra of CdS has maximum peak intensity at 511 nm, whereas that of Cd(S-Se) films consist of two peaks, one fixed at 494 nm and the other shifting to higher wavelength with increasing proportion of Se.
Maximum PL emission is observed for 0.7:0.3 combination of CdS to CdSe and hence this combination was used for further PL studies. PL emission spectra of Cd(S\text{0.7-Se}_{0.3}) films consist of two peaks that can be deconvoluted into two Gaussian curves one at 494 nm and the other at 559 nm [fig.-7]. Earlier workers [16] attributed these peaks to the radiative decay of free exciton and exciton-donor complexes found in presence of S / excess Cd respectively.

![PL emission spectrum of CdS film](image1.png)

![PL emission spectra of various Cd(S\text{1-x-Se}_{x}) films.](image2.png)

![Fig.-5 PL emission spectrum of CdS film](image3.png)

![Fig.-6 PL emission spectra of various Cd(S\text{1-x-Se}_{x}) films.](image4.png)

![PL emission spectra of Cd(S\text{0.7-Se}_{0.3}):CdCl\text{2} films at different concentrations of CdCl\text{2} are presented in fig.-10](image5.png)

![Fig.-7 Deconvolution of peaks for PL emission spectrum of Cd(S\text{0.7-Se}_{0.3}) film.](image6.png)

![Fig.-8 PL emission spectra of Cd(S\text{0.7-Se}_{0.3}):CdCl\text{2} films at different concentrations of CdCl\text{2}.](image7.png)

![Fig.-9 shows the PL emission spectra of Cd(S\text{0.7-Se}_{0.3}):CdCl\text{2,Sm} films at different molar](image8.png)

Fig.-9 shows the PL emission spectra of Cd(S\text{0.7-Se}_{0.3}):CdCl\text{2,Sm} films at different molar
concentrations of Sm(NO$_3$)$_3$. It is observed that out of the different molar concentrations of Sm(NO$_3$)$_3$ used, (0.001M; 0.005M; 0.01M and 0.05M), highest emission appears corresponding to 0.01M concentration. In Sm doped films showing maximum PL three new peaks appear at 563, 595 and 614 nm, as compared to the PL spectra of the base material. These peaks may be related to the transitions in Sm from the excited level $^4G_{5/2}$ to ground levels $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ respectively ($^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$) \[fig.-10\].

Fig.-9 PL emission spectra of Cd(S$_0.7$-Se$_{0.3}$):CdCl$_2$ films at different molar concentrations of Sm (NO$_3$)$_3$.

Trivalent samarium with 4$^6$ configuration has complicated energy level and various possible transitions between f-levels. The transition between these f-levels are highly selective and of sharp line spectra.

\[\text{Fig.-10} \quad \text{Valence Band}\]

\[\text{Conduction Band}\]

A proposed model of energy transfer from host to impurity level is shown in fig.-11.

4. Conclusions SEM studies show ball type structures, which may be due to layered growth. X-ray diffractograms of Cd(S-Se):CdCl$_2$,Sm films show the presence of CdS and CdSe along with lines of CdCl$_2$ and Sm. PL emission spectra are found to consist of peaks due to transitions in Sm levels.

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References:

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Dear Sir

I am happy to inform you that your paper entitled "Luminescent Properties of chemically deposited Sm²⁺ doped CdS-Se films" has been accepted for the NCRANT-2009 going to be held at SSCET, Junwani during 12 & 13 Jan. 2009.

The paper will be published by Narosa Publication, New Delhi. We want the proceeding of the conference during the conference.

See you soon in the conference venue on 12th of Jan 2009.

Seeking your kind co-operation and expecting your visit at SSCET.

Yours truly

Dr. Mohan L. Verma

Convener
Luminescent Properties of chemically deposited Sm$^{3+}$ doped CdS-Se films

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Abstract

Thin phosphor films of CdS-Se:CdCl$_2$,Sm$^{3+}$ were deposited by chemical deposition (CBD) process. Scanning electron microscopy (SEM), X-ray diffraction (XRD), optical absorption and Photoluminescence (PL) emission spectra were used to characterize the resulting films. The results of XRD indicated that crystallinity of films increased after annealing. Uniform and crack-free phosphor films were obtained by optimizing the composition of the chemicals used. The doped rare-earth ions (Sm$^{3+}$) showed its characteristic emission in the crystalline phosphor films due to an efficient energy transfer from host to them.

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1. Introduction

The energy levels of the lanthanide ions in a range of crystals were investigated and tabulated by Dicke et al in 1968 [1], and rare-earth ions have been extensively used as the active ions in phosphors for several decades. More recently, however, the development of flat panel displays and thin film electro-luminescent devices, or white light emitting diode, have emerged as the principal motivation for research into rare-earth luminescence, and the present article therefore concentrates on the way in which rare-earth luminescence has been exploited in this field [2-5]. 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 phosphor, based on “line-type” f-f transitions, can narrow to the visible, resulting in both high efficiency and a high lumen equivalent [6]. It is, therefore, urgent to find a stable, inorganic rare-earth-based phosphor with high luminescent efficiency. Further, application of high speed chemically deposited CdS_{0.26-Se_{0.74}} photoconductor as line image sensors and superior stability were reported by Yukami et al [7] and Rincon et al [8] respectively. Encouraged with such results, CdS-Se was selected as the base material for the present studies. Bhushan and coworkers [9-12] found enhancement in PL and PC due to doping of lanthanides in (Cd-Zn)S and (Cd-Pb)S. So for the present work Sm 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 thus presented Sm as an interesting activator.

The present paper reports results of SEM, XRD, optical absorption spectra and PL emission spectral studies of chemically deposited films of Sm^{3+} doped CdS-Se.

2. Experimental Procedure

The films were prepared by dipping microscopic glass slides of dimension 24 mm x 75 mm in a mixture of 1 M solution of cadmium acetate, thiourea, tri-ethanolamine, 0.01 M solutions of cadmium chloride, samarium nitrate and 0.42 M solution of sodium selenosulphate in appropriate proportions in presence of 30% aqueous ammonia. The pH value of the mixture was ~ 11. After deposition, the films were sprayed with double 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 0.1 to 0.9 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:112R horizontal Rotaflex and JEOL-JSM 5600 respectively.
3. Results and Discussions

3.1 Structural properties

The SEM profiles of Sm$^{3+}$ doped CdS-Se films chemically deposited on glass substrate at 60°C in WB and their annealed samples are presented in fig. 1(a), and (b) respectively. Ball type structure along with some voids are observed. 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$_{0.7}$-Se$_{0.3}$):CdCl$_2$,Sm(2 ml) [unannealed]](image1a)

![Fig. 1(b) SEM Micrograph of Cd(S$_{0.7}$-Se$_{0.3}$):CdCl$_2$,Sm(2 ml) [annealed]](image1b)

The X-ray profiles of Sm$^{3+}$ doped CdS-Se films chemically deposited on glass substrate at 60°C in WB and their annealed samples are presented in fig. 2(a) and (b) respectively.

![Fig. 2(a) X-ray diffractogram of Cd(S$_{0.7}$-Se$_{0.3}$):CdCl$_2$,Sm(2 ml) [unannealed]](image2a)

![Fig. 2(b) X-ray diffractogram of Cd(S$_{0.7}$-Se$_{0.3}$):CdCl$_2$,Sm(2 ml) [annealed]](image2b)
3.2 Spectral properties

Fig. 3 presents the optical absorption spectra of the Sm$^{3+}$ doped CdS-Se films recorded in the wavelength range 300-700 nm. An increase in the absorption corresponding to the onset of band-to-band transition is observed in both the curves. The absorption band for the host lattice is found between 300 and 500 nm. 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. There is no obvious absorption between 500 and 700 nm.

Fig. 4 presents the PL emission spectra of the Sm$^{3+}$ doped CdS-Se films. The peak positions in the PL emission spectra of Cd(S$_{0.7}$Se$_{0.3}$):CdCl$_2$,Sm (2 ml) film are obtained by deconvolution into Gaussian curves, these peaks are shown in fig.- 5. In addition to a peak at 494 nm, which has been attributed to the exciton bound to neutral donor levels formed by sulphur/excess Cd [15], there are three obvious emission peaks at 563, 595 and 614 nm that correspond to intra-4f-transitions $^4G_{5/2}$ $\rightarrow$ $^6H_{5/2}$, $^4G_{5/2}$ $\rightarrow$ $^6H_{7/2}$ and $^4G_{5/2}$ $\rightarrow$ $^6H_{9/2}$, shown in fig.- 6 [16]. Most of the f-f transitions of the trivalent lanthanides

![Absorption Spectra](image)

**Fig. 3** Absorption Spectra of:
1. Cd(S$_{0.7}$Se$_{0.3}$) and
2. Cd(S$_{0.7}$Se$_{0.3}$):CdCl$_2$,Sm

![PL emission spectra](image)

**Fig. 4** PL emission spectra of Cd(S$_{0.7}$Se$_{0.3}$):CdCl$_2$,Sm(2ml) film

![Deconvolution of PL emission spectrum](image)

**Fig. 5** Deconvolution of PL emission spectrum of Cd(S$_{0.7}$Se$_{0.3}$):CdCl$_2$,Sm (2ml) into Gaussian curves
are little affected by the environment. A few, however, are sensitive to the environment and become more intense. Such transitions have been called hypersensitive transitions [16]. This luminescence feature can yield structure information of a different character from that obtained by X-ray diffraction [17]. A proposed model of energy transfer from host to impurity level is shown in fig.- 7.

**Fig.- 6** Schematic diagram showing various emission transitions in \( \text{Cd(Sr}_{0.7}\text{-Se}_{0.3})\text{CdCl}_2,\text{Sm(2ml)} \) films

**Fig.- 7** Schematic diagram showing proposed energy transfer mechanism: 
(a) UV light absorbed within the host band gap;  
(b) relaxation to host defect states occurs; 
(c) energy transfer to crystal field states of the rare-earth ion, exhibiting PL

**Conclusions**

The chemically deposited Sm\(^{3+}\) doped CdS-Se films show layered growth morphology in the SEM studies. In XRD studies, existence of CdS, CdSe, CdCl\(_2\) and impurities are found. PL emission spectrum shows the presence of impurities in terms of transitions in these elements. Absorption studies also support their existence.

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References


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